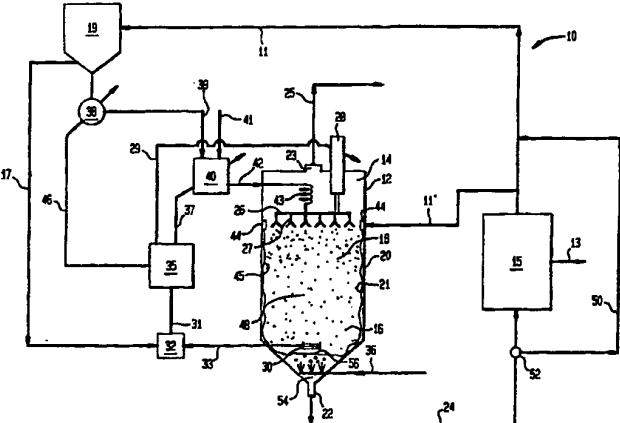


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(54) Title: METHODS AND DEVICES FOR MAKING INTERMEDIATE OXIDATION PRODUCTS BY CONTROLLING CONVERSIONS AND TEMPERATURES IN AN ATOMIZED LIQUID			
			
(57) Abstract			
<p>Methods and devices for making intermediate oxidation products by atomizing a first liquid containing a reactant into a gas containing an oxidant in a manner to form an intermediate oxidation product different than carbon monoxide and/or carbon dioxide. The oxidation is controlled by monitoring and adjusting the temperature and conversion at one or more different stages of the reaction. The oxidation is also controlled by monitoring and adjusting the pre-coalescing transient conversion (conversion taking place in the time interval between the formation of droplets and their coalescence into a mass of liquid) of first reactant to oxidation product just before the droplets coalesce into a mass of a second liquid, or by monitoring the pre-coalescing temperature (temperature of the droplets just before they coalesce into a mass of liquid), or transient temperature difference (difference between the pre-coalescing temperature and the temperature of the droplets just before atomized), or transient temperature sub-difference (temperature difference between two positions within the reaction zone), or combination thereof. This invention provides waste minimization and considerable environmental improvement among other advantages.</p>			

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Description

5    Methods and Devices for Making Intermediate Oxidation Products by Controlling  
Conversions and Temperatures in an Atomized Liquid

Technical Field

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This invention relates to methods and apparatuses for making reaction products, and especially intermediate oxidation products, wherein a first reactant incorporated in an atomized liquid reacts with a gas containing a second reactant, and especially an oxidant, under controlled conditions.

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Background Art

Reactions where a first reactant, dissolved in a liquid, reacts with a second reactant contained in a gas under increased surface area conditions are known to the art. Such reactions are carried out in devices as scrubbers, burners, reaction vessels, and the like, for example.

Atomization of liquids into a gaseous atmosphere is one of the above mentioned techniques described in the art. The atomization techniques for conducting reactions, disclosed in the art so far, are rather crude and lack innovative features for controlling such reactions with respect to desired reaction product if the reaction product is an intermediate, yield in reaction product, conversion and conversion rate, temperature profiles in the reaction zone, average droplet size or diameter, evaporation rates, and the like. Actually in most, if not all, cases, the reaction product is substantially the final product expected under the crude overall conditions of the reaction. For example, in the case of a burner, where a fuel is atomized into an atmosphere of an oxygen-containing gas (such as air for example), the final product of

reaction is carbon dioxide, with desired minimization of carbon monoxide and nitrogen oxides as much as possible. In another example, a scrubber for removing acidic compounds from a gas may use an atomized liquid containing alkali or alkaline earth compounds which react with the acidic compounds in the gas to form the corresponding salts. In still another example, ammonia and phosphoric acid react under atomization conditions to form ammonium orthophosphate, which is a final reaction product.

On the other hand, reactions which are geared to produce intermediate products, especially in the case of oxidations, are not run under atomization conditions, since atomization promotes complete reactions to a final product. For example, oxidation of cyclohexane to adipic acid, or oxidation of p-xylene to terephthalic acid, have not been reported to be conducted under atomization conditions, and there is no incentive in the art to do so, since burning of cyclohexane to carbon dioxide has been expected to take place under such conditions. However, the inventors have discovered that in the presence of unexpected intricate critical controls and requirements of the instant invention, intermediate reaction or oxidation products, such as adipic acid, phthalic acid, isophthalic acid and terephthalic acid, for example, may be advantageously obtained under atomization conditions.

20

The following references, among others, describe processes conducted in intermixing liquid with gaseous materials, mostly under increased surface area conditions.

25 U.S. Patent Nos. 5,399,750 (Brun et al.); 5,396,850 (Conochie et al.); 5,312,567 (Kozma et al.); 5,244,603 (Davis); 5,270,019 (Melton et al.); 5,170,727 (Nielsen); 5,123,936 (Stone et al.); 5,061,453 (Krippl et al.); 4,423,018 (Lester, Jr. et al.); 4,370,304 (Hendriks et al.); 4,361,965 (Goumondy et al.); 4,308,037 (Meissner et al.); 4,065,527 (Graber); 4,039,304 (Bechthold et al.); 3,928,005 (Laslo); 30 3,677,696 (Helsinki et al.); 3,613,333 (Gardenier); 2,980,523 (Dille et al.); 2,301,240 (Baumann et al.); 2,014,044 (Haswell); 1,121,532 and (Newberry).

Currently, oxidation reactions for the production of organic acids, including

but not limited to adipic acid, are conducted in a liquid phase reactor with reactant gas sparging. The reactant gas in these cases is typically air, but may also be oxygen. Sufficient reactant gas, with or without non-reactive diluents (e.g., nitrogen), is sparged - at relatively high rate - so that the liquid reaction medium is aerated to maximum capacity (typically 15-25 % aeration). The relatively high sparging rates of reactant containing gas feed (hereinafter referred to as "reactant gas"), associated with this conventional approach, have several drawbacks:

- 10        o Costly reactant gas feed compressors are required to compress makeup reactant gas for sparging. These are expensive to install and operate (high electric or steam consumption), and have many utility problems resulting in excessive plant downtime.
- 15        o The required high gas rate makes it extremely difficult to control oxygen content in the reactor at low concentrations (due to the high reactor gas turnover rate).
- 20        o The required high gas rate makes it extremely difficult to control reaction temperature at low production rates (i.e., high turndown rate) for a given sized reactor system. This occurs because the gas used for sparging removes energy from the reaction system by volatilizing reaction liquid and liquid solvent – this volatilization effect is quite significant at the relatively high temperatures commonly associated with and required for oxidation reactions. Unless carefully balanced by an exothermic heat of reaction, this volatilization will act to substantially lower the temperature of the liquid content of the reactor. Thus, a properly sparged system can be designed for good temperature control at medium to high production rates, but will suffer temperature loss and loss of temperature control at significant turndown rate.
- 30        o High reactant gas feed rate results in relatively high reactor non-condensable off-gas rate. Non-condensable off-gases must either be totally purged to atmosphere, or - if oxygen content is high - partially purged and

partially recycled to the reactor. The use of air as a reactant gas feed has drawbacks because it results in high rate of purge to the atmosphere -- this is undesirable because this purge must first be cleaned in very expensive off-gas cleanup facilities in order to meet ever more stringent environmental requirements. The use of oxygen-only gas feed to the reactor may be undesirable because high sparging requirements result in low oxygen conversion in the reactor; low conversion results in high oxygen concentration within the reactor; and high oxygen concentration within the reactor may result in excessive over-oxidation of liquid reactants and liquid solvents with attendant high chemical yield loss (i.e., burning these to carbon monoxide and carbon dioxide). If the oxygen in the reactor is diluted with recycle nitrogen or gaseous-recycle inerts, then both high recompression investment and costs, and recompression utility problems are introduced.

15        The current technology also suffers from a relatively low ratio of gas-liquid surface area to liquid reaction mass. The presently available art does not maximize this ratio. In contrast, the present invention maximizes said ratio in order to:

20        increase reaction rate by increasing the mass transfer rate of gaseous reactants (oxygen) to liquid reaction sites; and

enable economic operation at relatively low oxygen concentration in the gas phase.

25        Operating at lower oxygen concentration with acceptable conversion rates in the reactor improves yield by reducing over-oxidations, and eliminates safety (explosion) problems associated with operation in the explosive oxygen/fuel envelope. In the current technology, reducing oxygen content below traditional levels would result in a non-economic reduction in reaction rate. However, a 30 significant increase in the aforementioned ratio - relative to current levels - would offset this rate reduction thereby enabling economic operation at reduced oxygen concentration in the reactor.

Another problem with the current technology is the sometimes formation of large agglomerations of insoluble oxidation products in the reactor. These can build up on reactor walls resulting in decreased available reaction volume, and in unwanted by-product formation due to over-exposure of said accretions to reaction 5 conditions (e.g., high temperature) in oxygen-starved micro-reactor environments. These can also form large diameter, heavy solids in the reactor which can result in damage to expensive reactor agitator shafts and agitator seals resulting in costly repairs and high utility wear-problems. Finally, the current technology often requires expensive agitation shafts and seals capable of withstanding corrosive chemical 10 attack and containing high system pressures.

Substituting gas-phase reaction systems for liquid-phase reactors introduces new problems, chief among which is the difficulty of identifying a cost-effective, efficient, non-plugging, long-lived catalyst system. Liquid-phase catalyst systems 15 are well-developed and well-understood. Unfortunately, these are non-volatile. Using a non-volatile catalyst in a gas-phase reaction system must necessarily often be subject to severe plugging problems as most organic acids resulting from oxidation reactions are non-volatile solids -- unless dissolved in a liquid reaction medium.

20

There is a plethora of references dealing with oxidation of organic compounds to produce acids, such as, for example, adipic acid.

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The following references, among the plethora of others, may be considered as representative of oxidation processes relative to the preparation of diacids.

U.S. Patent Nos. 5,321,157 (Kollar); 5,221,800 (Park et al.); and 5,463,119 (Kollar).

30

The following references, among others, describe oxidation processes conducted in multi-stage and multi-plate systems.

U.S. Patent Nos. 3,987,100 (Barnette et al.); 3,957,876 (Rapoport et al.);

and 3,530,185 (Pugi).

None of the above references, or any other references known to the inventors disclose, suggest or imply, singly or in combination, oxidation or other 5 types of reactions to intermediate oxidation or other products under atomization conditions subject to the intricate and critical controls and requirements of the instant invention as described and claimed.

10 Disclosure of the Invention

As aforementioned, the present invention relates to methods and devices of making intermediate oxidation products, wherein a first reactant incorporated in an atomized liquid reacts with a gas containing an oxidant under controlled conditions.

15 More particularly, this invention pertains a method of preparing an intermediate oxidation product from a first liquid containing a first reactant and a gas containing an oxidant;

wherein the improvement comprises the steps of:

20

(a) atomizing the first liquid to form a plurality of droplets in the gas at an atomization temperature and at an atomization distance from a mass of a second liquid;

25

(b) causing a substantially non-destructive oxidation at an oxidation pressure between the first reactant and the oxidant to form the intermediate oxidation product;

30

(c) coalescing the droplets into the mass of the second liquid; and

(d) controlling a parameter or determinant selected from a group consisting of pre-coalescing temperature of the droplets, transient temperature difference of the droplets, transient temperature sub-difference of the droplets, pre-

coalescing transient conversion, and a combination thereof, to be within respective predetermined ranges, before said droplets coalesce into the second liquid.

5 The intermediate oxidation product may be then separated from the second liquid.

Pre-coalescing temperature is the temperature of the droplets just before they coalesce into the second liquid.

10 Transient temperature difference is the difference of temperature of the droplets between the pre-coalescing temperature and the atomization temperature. Atomization temperature is the temperature of the first liquid in the atomizer, just before the first liquid has been atomized.

15 Atomization distance is the distance between the atomizer and the mass of second liquid.

According to this invention, transient temperature sub-difference is a  
20 difference in droplet temperature between a point positioned towards the atomization location and a point positioned toward the second liquid location, within the path that the droplets follow. Transient temperature sub-differences are useful because they give information regarding the temperature profile within the reaction chamber and additional data relative to the progress of the reaction. Their use is  
25 within the scope of this invention. Further, according to this invention, a transient temperature sub-difference between a point close to the atomizer and a point close to the second liquid may be used in lieu of the transient temperature difference, as defined above.

30 Pre-coalescing transient conversion is the conversion taking place from the point that the first liquid is atomized to form first droplets to the point just before the first droplets coalesce to a mass of liquid, as described hereinwith. This occurs in just one cycle of droplet formation and droplet coalescence. The word "conversion"

without any modification refers to conversion of a reactant to a reaction product. Thus conversion, at any point during a reaction, is defined as the percentage ratio of moles of reaction product formed during the reaction to the total moles of reactant in the feedstock, multiplied by the reciprocal of the number of moles of reaction

5 product produced theoretically when one mole of reactant is completely converted to said reaction product.

Pre-coalescing temperature of the droplets, transient temperature difference of the droplets, transient temperature sub-difference of the droplets, and pre-10 coalescing transient conversion are called determinants since they are determining parameters regarding control of the oxidation. Thus, the oxidation is driven by different variables, as described in detail hereinbelow, in a manner that one or more of the following are caused to occur: the pre-coalescing temperature attains a value within a predetermined pre-coalescing temperature range, the transient temperature difference attains a value within a predetermined transient temperature difference range, any transient temperature sub-difference attains a value within a15 predetermined transient temperature sub-difference range, and the conversion attains a value within a predetermined pre-coalescing transient conversion range.

20 Corrections have to be made for different factors which may influence the transient temperature difference one way or another, by well known to the art techniques, involving measurements and calculations. Since changes in the transient temperature difference may be more important than its absolute value, high accuracy in the measurements and calculations is not required in most25 occasions. Similar corrections and techniques may be employed for the rest of the determinants.

The determinant which happens to be outside its respective predetermined range and further away from its respective most preferred set value takes preferably30 precedence or it is said to prevail. By this it is meant that the computerized controller, as described in the embodiments hereinbelow, temporarily assigns lower priority to data from the other determinants, and handles first the data received regarding the prevailing determinant. After the prevailing determinant has been

closer to its respective most preferred set value than another determinant, the other determinant takes precedence or prevails. Thus, after all determinants are within their respective predetermined value ranges, the determinant further away from its respective most preferred set value takes precedence or prevails until all

5 determinants attain their most preferred set value. No variables are changed at this point until one determinant deviates, at which point the sequence described above is initiated again, thus maintaining all determinants as close as possible to their respective preferred set values. This sequence is followed continuously with the goal to maintain all determinants within their respective predetermined ranges at all

10 times, always driving each determinant toward the most preferred set value. When a determinant has to be chosen for taking precedence over another determinant, whether characterized by the same or different units, each respective predetermined range is divided in 100 arbitrary units, arbitrarily assumed to be equivalent in both cases, and all values are prorated within these equivalent

15 arbitrary units (both inside each range and outside each range).

It is important to note that according to this invention, appropriate overriding program rules may be used to override the above sequences, especially in occasions involving safety matters. For example, if the pre-coalescing temperature

20 or the transient temperature difference or any transient temperature sub-difference start rising at a rate faster than a preset value, the corresponding determinant should take over, regardless of precedence as described above, and cause commensurate change in one or more variables at a high enough rate to offset said rise on time, before any catastrophic outcome.

25 In addition, monitoring carbon monoxide and carbon dioxide in the off-gases is a prudent precaution, since unexpected or higher than normal amounts of carbon monoxide and/or carbon dioxide signify poorly controlled or uncontrolled oxidation. Similar overriding rules, applied by the controller described below, help prevent poor

30 yields, poor conversions, and even explosions.

Control of the parameter or determinant may be performed by a step selected from a group consisting of changing the predetermined level of catalyst in the

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droplets, changing the atomization temperature of the droplets, changing the reaction pressure in the reaction chamber, changing the atomization distance, changing the average droplet diameter, changing the first flow rate (the rate at which the droplets are produced), changing the second flow rate (the rate at which the gas flows), changing the volatilization rate at which volatile ingredients in the first liquid volatilize, changing the first content (content of first reactant in the first liquid), changing the second content (content of oxidant in the gas), and a combination thereof.

10 The pre-coalescing transient conversion may be monitored by a chromatographic method.

Preferably, a major portion of the oxidation product is an organic compound, the first reactant comprises an organic compound, and the oxidant is oxygen, and 15 even more preferably,

the first reactant comprises a compound selected from a group consisting of cyclohexane, cyclohexanone, cyclohexylhydroperoxide, cyclohexanol, o-xylene, m-xylene, p-xylene, a mixture of at least two of cyclohexane, cyclohexanone, cyclohexanol, and cyclohexylhydroperoxide, and a mixture of at least two of o-xylene, p-xylene, and m-xylene.

20 the oxidant comprises oxygen; and

25 a major portion of the intermediate oxidation product comprises a compound selected from a group consisting of adipic acid, cyclohexanol, cyclohexanone, cyclohexylhydroperoxide, phthalic acid, isophthalic acid, terephthalic, a mixture of at least two of adipic acid, cyclohexanone, cyclohexanol, and cyclohexylhydroperoxide, and a mixture of at least two of phthalic acid, 30 isophthalic acid, and terephthalic acid.

In the case that the intermediate oxidation product is a solid, the method may involve a step of separating the intermediate oxidation product from the second liquid

by filtration.

Spraying is the preferred way of atomizing the first liquid from a point over the surface of the second liquid at the atomization distance, by preferably an airless technique.

The method may preferably further comprise a step of internally condensing condensables substantially under reaction pressure. Also, the method of non-destructive oxidation may be conducted in a reaction zone surrounded by a thick film or curtain of liquid.

The preferable predetermined pre-coalescing transient conversion range is 0.05% to 80%, the predetermined pre-coalescing temperature range is 50 to 250° C, and the transient temperature difference is in the range of 0.1 to 100° C.

15

The invention also pertains a device for preparing a reaction product from a first liquid containing a first reactant and a gas containing a second reactant comprising a reaction chamber having an upper end, a lower end, a wall, and a reaction zone, in which zone the first liquid is brought in contact with the gas for reacting at a reaction pressure, wherein the improvement comprises:

25

(a) an atomizer disposed within the reaction chamber adapted to break the first liquid into a plurality of droplets within the gas at an atomization temperature in a manner that the droplets coalesce on a mass of a second liquid containing reaction product, the droplets having a pre-coalescing temperature before they coalesce, the mass of the second liquid having a second liquid surface, the atomizer being away from said second liquid surface at an atomization distance;

30

(b) a monitor selected from a group consisting of a first temperature monitor for measuring the atomization temperature, a second temperature monitor for measuring pre-coalescing temperature and/or transient temperature difference and/or any transient temperature sub-difference, a conversion

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detector for monitoring pre-coalescing transient conversion of the first reactant to reaction product in the droplets before the droplets coalesce onto the mass of the second liquid, and a combination thereof; and

5

(c) a controller connected to at least one of the first temperature monitor, the second temperature monitor, and the conversion detector in order to obtain respective information, the controller being adapted to point a parameter or determinant selected from a group consisting of pre-coalescing temperature of the droplets, transient temperature difference of the droplets, transient temperature sub-difference of the droplets, pre-coalescing transient conversion, and a combination thereof, toward respective predetermined ranges.

10

The device may also comprise a separator communicating with the reaction chamber for separating the reaction product from the second liquid, and/or a recirculation branch for recirculating at least part of the second liquid into the first liquid.

15

The conversion detector preferably comprises a chromatography apparatus.

The atomizer is preferably disposed toward the upper end, and directed toward the lower end at the atomization distance. It is preferably airless.

20

Brief Description of the Drawings

The reader's understanding of this invention will be enhanced by reference to the following detailed description taken in combination with the drawing figures,

25  
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wherein:

FIGURE 1 illustrates schematically a preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion is achieved by

changing the atomization distance through a movement of the atomizer.

5 FIGURE 1A illustrates schematically a preferred embodiment of the present invention, wherein control of pre-coalescing temperature and/or pre-coalescing transient conversion is achieved by changing the atomization distance through a movement of the atomizer.

10 FIGURE 2 illustrates schematically another preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion is achieved by changing the atomization temperature.

15 FIGURE 2A illustrates schematically another preferred embodiment of the present invention, wherein control of pre-coalescing temperature and/or transient temperature difference is achieved by changing the atomization temperature.

20 FIGURE 3 illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion is achieved either by changing the pressure in the reaction chamber, or by changing the second flow rate, or by changing the second content.

25 FIGURE 3A illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing temperature and/or of transient temperature difference is achieved either by changing the pressure in the reaction chamber, or by changing the second flow rate, or by changing the second content.

30 FIGURE 4 illustrates schematically still another preferred embodiment of the present invention, wherein control of transient pre-coalescing conversion is achieved by changing the first content.

35 FIGURE 4A illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing temperature is achieved by changing the first content.

5 FIGURE 5 illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion is achieved by changing the droplet size or diameter.

10 FIGURE 5A illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing temperature is achieved by changing the droplet size or diameter.

15 FIGURE 6 illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion is achieved by changing the first flow rate.

20 FIGURE 6A illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing temperature and/or transient temperature difference is achieved by changing the first flow rate.

25 FIGURE 7 illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion is achieved by changing the volatilization rate.

30 FIGURE 7A illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing temperature and/or transient temperature difference is achieved by changing the volatilization rate.

FIGURE 8 illustrates schematically still another preferred embodiment of the present invention, wherein control of pre-coalescing transient conversion or of pre-coalescing temperature is achieved by changing the atomization distance through moving the level of the surface of the second liquid.

FIGURE 9 illustrates schematically the sample collector utilized in the embodiments of Figure 8.

FIGURE 10 illustrates schematically a filter arrangement comprised in the separator according to another preferred embodiment of the present invention.

5 FIGURE 11 illustrates schematically still another preferred embodiment of the present invention, wherein an eductor is utilized to recirculate non-condensable off-gases, a condenser is used to condense condensibles, and part of the condensibles return to the reaction chamber, where a thick film or curtain is formed for preventing solids buildup on the walls.

10 FIGURE 12 illustrates schematically still another preferred embodiment of the present invention, wherein a pump is utilized to recirculate non-condensable off-gases, a condenser is used to condense condensibles, and part of the condensibles return to the reaction chamber, where a thick film or curtain is formed for preventing 15 solids buildup on the walls.

FIGURE 13 illustrates schematically still another preferred embodiment of the present invention, wherein both condensibles and non-condensibles leave the reactor through the lower end.

20 FIGURE 14 illustrates schematically still another preferred embodiment of the present invention, wherein a cooling mantle surrounds the reaction chamber.

25 FIGURE 15 illustrates schematically still another preferred embodiment of the present invention, wherein a cooling coil performs condensation inside the reaction chamber.

FIGURE 16 illustrates schematically still another preferred embodiment of the present invention, wherein condensation inside the reactor is performed by spraying 30 a cooling liquid along with atomization of the first liquid.

FIGURE 17 illustrates schematically still another preferred embodiment of the present invention, wherein condensation inside the reactor is performed by spraying

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a cooling liquid towards the walls of the reaction chamber.

FIGURE 18 illustrates schematically a reaction chamber having thermocouples for measuring transient temperature sub-difference.

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FIGURE 19 illustrates schematically a preferred embodiment of the present invention, wherein oxidation rate of the reaction in a reaction chamber is controlled by adjusting the temperature and or conversion of first reactant to intermediate oxidation product at different locations of the system.

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#### Best Mode of Carrying out the Invention

As aforementioned, the present invention relates to methods of making intermediate oxidation products, wherein a first reactant incorporated in an atomized liquid reacts with a gas containing an oxidant, under controlled conditions. According to the present invention, the atomization conditions are subject to intricate critical controls and requirements as described and claimed hereinbelow.

The present invention enables economic oxidation reactions at improved yield with reduced compression costs and investment, using proven catalyst systems, with reduced off-gas waste-stream discharge to the atmosphere, with reduced off-gas cleanup investment and costs, without solids plugging or buildup problems, with high utility, high conversion rates, and with reduced oxygen concentrations in the reaction chamber.

The ability to operate at lower oxygen concentration, made possible by this invention, with acceptable conversion rates in the reactor improves yield by reducing over-oxidations, and may eliminate safety (explosion) problems associated with operation in the explosive oxygen/fuel envelope by operating in the non-explosive oxygen/fuel envelope.

As it will become clear in the course of this discussion, unlike in the

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conventional technology which utilizes sparging of oxidizing gases through mechanically agitated liquids containing reactants to be oxidized, there is no reaction chamber agitator and no agitator seals. This process simplification is made possible by the unique reaction environment provided by this invention, and is highly desirable  
5 as it reduces cost, investment, and improves plant utility compared to the conventional technology.

Since according to the present invention the oxidation is conducted within the droplets, which are in a liquid phase, the process still maintains the advantage of  
10 being able to employ efficient liquid-soluble catalyst systems, with the added advantage of attaining reaction conditions almost as efficient as those encountered in a homogeneous gaseous phase. Reactions in a gaseous phase would require costly and uncertain gas-phase catalysts or solid-phase catalyst systems.

15 Further, this invention enables a low off-gas waste-stream rate, if so desired, which reduces the off-gas waste-stream rate to the environment, and reduces off-gas cleanup investment and costs. The low off-gas waste-stream rate may be made possible with a near-stoichiometric gaseous oxygen feed combined with high conversion rates and/or chemical yields, for example.

20 In the conventional technology, reaction chamber non-condensable off-gas is commonly purged to the atmosphere without partial recycle back to the reaction chamber. This results in increased oxygen consumption and related cost, but is done to avoid high, non-economic recompression costs and investment. In the  
25 conventional technology, recompression costs and investment are high due to a high non-condensable load, and high recycle pressure requirement.

When, according to the methods and devices of this invention, condensation is employed at a stage before the pressure drop (internal condensation), as shown in  
30 the embodiment of Figure 11 (before valve 864) for example, the increased oxygen consumption and related cost, and the high, non-economic recompression costs and investment associated with the conventional technology are avoided. According to this embodiment, it is possible to recycle oxygen-containing off-gas back to the

reaction chamber with relatively low or no recompression requirement and cost. The recycle may be even eliminated without incurring significant adverse economic impact. When condensation is employed at such a stage, the recompression requirement is minimal - compared to the conventional technology - due to the low non-condensable off-gas rate, especially when near-stoichiometric oxygen feed is used. The low non-condensable off-gas rate is due to the combination of near-stoichiometric oxygen feed, with one or more of high oxygen conversion rate, high chemical yield, and internal condensation, enabled and provided for by the instant invention.

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It should be stressed that internal condensation may take place either outside or inside the reaction chamber, as illustrated later. Internal condensation is condensation which takes place within the system, before the pressure is relieved. External condensation is condensation which takes place outside the system, after the pressure has been relieved. Inside or internal inside condensation is condensation which takes place inside the reaction chamber. Outside condensation or internal outside condensation is condensation which takes place inside the system before the pressure is relieved, but outside the reaction chamber.

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According to the instant invention, when near-stoichiometric oxygen feed is desired, it is achievable by the high conversion of the oxygen feed to the reaction chamber per pass, hence needing little recycle requirement. The high chemical yield results in low non-condensable by-product formation, thereby significantly reducing off-gas purge load generated in the reaction chamber. Reduced off-gas purge load in turn reduces oxygen purge from the reaction chamber. Reduced oxygen purge from the reaction chamber minimizes oxygen recycle requirement. The implementation of internal condensation further reduces recompression requirement, as internal condensation outside the reactor reduces condensable vapor recycle requirement, and the implementation of internal condensation inside the reactor reduces oxygen recycle requirement further still. Thus, internal condensation, especially inside the reactor, significantly reduces oxygen physical yield-loss. In the limit, internal condensation, complete oxygen conversion per pass, i.e., stoichiometric oxygen feed, and zero non-condensable by-product formation results

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in substantially zero oxygen physical yield loss and substantially zero recompression requirement. Due to the low non-condensable off-gas rate made possible when internal condensation is employed, it is significantly less costly (compared to the conventional technology) to forego recycle.

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In this invention, solids buildup in the reaction chamber is prevented by washing the walls of the reaction chamber with preferably cooler, preferably catalyst-free liquid solvent, or with preferably catalyst-free liquid reactant, or with a mixture thereof. All surfaces of the reaction chamber, or a certain portion of those surfaces 10 prone to solids buildup, may be washed in this manner. The wash liquid may be sprayed onto the surfaces so washed, or may be generated in situ as a result of internal inside condensation. Solids buildup is prevented because the solids in contact with these surfaces are continuously washed out of the reaction chamber. Furthermore, reaction in the wash-liquid is greatly minimized by the lower 15 temperature or absence of catalyst, the short hold-up-time or a combination thereof. All solids produced in the reaction chamber are removed from the reaction chamber with the wash liquid.

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According to this invention, huge improvements in diffusion rates may be made by using ultra-high ratios of gas/liquid interfacial area to liquid reaction volume, which are obtained by converting the bulk stirred liquid phase into spray droplets of controlled small size within a continuous gas-phase.

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The significant reduction in the oxygen concentration in the gas-phase, concurrent with still maintaining desirable high reaction rates, made possible by this invention, is extremely desirable because it acts to improve yield by reducing over-oxidation, improve safety by enabling operation further away from the oxygen/fuel explosive envelope, and minimize the amount of oxygen swept from the reaction 30 chamber.

The ways to control average droplet diameters in atomization is well-known to the art, and it includes, but is not limited to, nozzle design, variable nozzle

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characteristics, pressure of atomized material, pressure of gas if gas is used for the atomization process, and the like.

According to this invention, pre-coalescing temperature and/or transient

5 temperature difference, and/or pre-coalescing transient conversion can be controlled, for example, by regulating the oxygen concentration in the reaction chamber. This is to be done by using oxygen as the limiting reagent. In this instance, the rate of oxygen feed to the reaction chamber would be increased or decreased as required to control pre-coalescing temperature and/or transient

10 temperature difference and/or pre-coalescing transient conversion. Pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are increased - holding all other variables constant - by increasing oxygen feed rate, and thereby increasing oxygen concentration in the reaction chamber. Pre-coalescing temperature and/or transient temperature difference

15 and/or pre-coalescing transient conversion are decreased - holding all other variables constant - by decreasing oxygen feed rate, and thereby decreasing oxygen concentration in the reaction chamber.

Further, pre-coalescing temperature and/or transient temperature difference

20 and/or pre-coalescing transient conversion are increased - holding all other variables constant - by increasing the concentration of catalyst in the liquid feed to the reaction chamber. Pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are decreased - holding all other variables constant - by decreasing the concentration of catalyst in the liquid feed to the reaction chamber.

In addition, pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are increased - holding all other variables constant - by increasing the hold-up time of the liquid feed in the

30 reaction chamber. Pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are decreased - holding all other variables constant - by decreasing the hold-up time of the liquid feed in the reaction chamber. Hold-up time of the liquid feed in the reaction chamber is

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controlled by varying the height of the gas-phase through the droplets fall. Hold-up time is increased by increasing the height, and decreased by decreasing the height. The height may be controlled in several ways. For example, it may be controlled by:

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- o Raising or lowering the height of the droplet spray nozzle or nozzles.
- o Raising or lowering the height of a liquid pool at the liquid level at the end of the vertical reaction chamber. The height of the liquid pool can be determined and controlled by a variety of ways well known to the art.

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Also, pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are increased - holding all other variables constant - by decreasing the size of the liquid droplets in the reaction chamber. Pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are decreased - holding all other variables constant - by increasing the size of the liquid droplets in the reaction chamber. Droplet size inversely affects pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion by controlling oxygen mass transfer into the liquid reaction media. Since the ratio of surface area to volume for a spherical droplet is inversely proportional to the diameter of a droplet, and since oxygen transport from the gas-phase is directly proportional to the surface area of a droplet, then the ratio of oxygen mass transport to the liquid volume contained in a droplet varies inversely with the diameter of the droplet. Therefore, the relative oxygen mass transfer for larger droplets is smaller than that for smaller droplets, and pre-coalescing temperature and/or transient temperature difference and/or pre-coalescing transient conversion are correspondingly reduced when all other variables are held constant.

Since reaction rates are faster at higher temperatures, in this invention, pre-coalescing transient conversion is increased - holding all other variables constant - by increasing the pre-coalescing temperature and/or the transient temperature difference of the liquid droplets. Conversion is decreased - holding all other

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variables constant - by decreasing the pre-coalescing temperature and/or the transient temperature difference of the liquid droplets in the reaction chamber.

According to this invention, the heat of reaction may be removed from the

5 liquid reaction mass as vaporized liquid reactant and vaporized liquid solvent.

These vaporized materials may be condensed either outside or inside the reaction chamber as it will be discussed hereinbelow. Removal of heat inside the reaction chamber may be conducted for example by using condensation sprays, or condensation surfaces, or a combination thereof.

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According to this invention, a controller points the pre-coalescing temperature of the droplets, transient temperature difference of the droplets, transient temperature sub-difference of the droplets, pre-coalescing transient conversion in the droplets, or a combination thereof, toward predetermined ranges.

15 By this, it is meant that the controller is adapted to change one or more variables, such as the preferable variables listed as examples hereinwith, so that said change will favor a respective change in the pre-coalescing temperature, or transient temperature difference, or pre-coalescing transient conversion, or a combination thereof toward the predetermined range.

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The pre-coalescing temperature and transient temperature difference depend on the particular oxidation. As an example, in the case of oxidation of cyclohexane to adipic acid, the preferable range of pre-coalescing temperature is 50 - 150° C, more preferably 80 - 130° C, and even more preferably 90 - 120° C. The

25 preferable transient temperature difference is in the range of 0.1 to 100° C, more preferably 5 - 100° C, more preferably 10 - 50° C, and even more preferably 15 - 35° C. For the preparation of phthalic, isophthalic and terephthalic acids, from o-

xylene, m-xylene and p-xylene, respectively, the preferred pre-coalescing

temperature is in the range of 50 to 250° C. Appropriate ranges of pre-coalescing

30 temperature, transient temperature difference, and predetermined pre-coalescing transient conversion may be determined without undue experimentation for other oxidations or miscellaneous conditions of the same oxidation.

The preferable predetermined pre-coalescing transient conversion range is 0.05% to 80%.

Depending on the reaction characteristics, some variables may be more or less effective and efficient in causing changes to the re-coalescing temperature, or transient temperature difference, or pre-coalescing transient conversion, or a combination thereof. It is possible in some occasions that changes in one variable may not be capable to bring the pre-coalescing temperature, or transient temperature difference, or pre-coalescing transient conversion, or a combination thereof within the predetermined ranges. In such cases, the controller is preferably adapted or programmed to select and change one or more additional variables in order to receive the desired result.

In the description of the preferred embodiments of the instant invention, it is assumed for purposes of clarity that the particular variable under consideration is capable by itself to bring the pre-coalescing temperature, or transient temperature difference, or pre-coalescing transient conversion, or a combination thereof within the predetermined ranges. This is generally true, provided that for a particular reaction, conducted in the devices and by the methods of this invention, the most efficient variable(s) has been selected to be controlled by the controller. It should be understood, however, that the selection of one or more additional variables is well within the scope of this invention.

The temperatures may be monitored by any temperature-measuring devices, such as for example thermocouples, IR thermometers, and the like.

It is important to note that according to this invention, appropriate overriding program rules may be used to override the normal program of the controller, especially in occasions involving safety matters. For example, the temperature in the reaction chamber may preferably be monitored, and if it is found to start rising at a rate faster than a preset value, the controller should cause commensurate changes in one or more variables at a high enough rate to offset said rise timely, before any catastrophic outcome.

In addition, monitoring carbon monoxide and carbon dioxide in the off-gases is a prudent precaution, since unexpected or higher than normal amounts of carbon monoxide and/or carbon dioxide signify poorly controlled or uncontrolled oxidation.

5 Similar overriding rules applied by the controller help prevent poor yields, conversions, and even explosions.

In the following description, the droplets have an average droplet diameter and they are produced at a desired first flow rate, the gas flows at a second flow rate, the droplets may contain volatile ingredients volatilizing at a volatilization rate, the first liquid contains a first reactant at a first content, the gas contains oxidant at a second content. The ratio of the oxidant to the inert or other gas determines the content of oxidant in the gas.

15 Also, in the following description, pre-coalescing transient conversion is the conversion of first reactant to intermediate oxidation product as droplets of first liquid travel from the atomizer to the sample collector. It should be understood that information regarding the amounts of first reactant and oxidation product, if present, are monitored in the first liquid and they are provided to the computerized controller 20 through the conversion monitor along with information regarding the percent moles of intermediate oxidation product in the sample collector. This whole information is collectively called pre-coalescing transient conversion information. The analyses and/or computations from different lines are conducted by well known to the art techniques, and they have been omitted from the Figures for purposes of clarity.

25 More specifically the pre-coalescing transient conversion is defined as the ratio  $[(O^2 - O^1) \times 100] / [R^1 \times n]$ , where:

$O^1$  is the percent moles of intermediate oxidation product in the first liquid;

30  $O^2$  is the percent moles of intermediate oxidation product as provided to the conversion monitor by the sample collector;

$R^1$  is the percent moles of first reactant in the first liquid; and

n is the number of moles of intermediate oxidation product produced when one mole of first reactant is completely converted to said intermediate oxidation product.

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The inventors have recognized that, in the case of atomizing reactors, pre-coalescing temperature, transient temperature difference, and pre-coalescing transient conversion are of essence for controlling oxidation reactions, and not just the overall temperature or conversion over the whole process, as employed so far in 10 the art. Control of pre-coalescing temperature, or transient temperature difference, or both with or without control of pre-coalescing transient conversion, not only helps in improving the yield, but in addition it helps in avoiding reactions leading to complete oxidation, combustion, or even explosion.

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In one embodiment of the present invention, better shown in Figure 1, there is depicted a device 10 for preparing an intermediate oxidation product from a first liquid containing a first reactant and a gas containing a second reactant. The device 10 comprises a reaction chamber 12, which chamber has an upper end 14, a lower end 16 and a reaction zone 18. The reaction chamber 12 also has a wall having an 20 inside surface 21. The chamber 12 is preferably of cylindrical shape turning to conical at the vicinity of the lower end 16, and finally leading to a liquid outlet 22 connected to an outlet line 24. The outlet line 24 leads to a separator 15 where the intermediate oxidation products are separated from reactants following line, and unreacted reactants, usually containing various amounts of intermediate oxidation 25 products, solvents, catalysts, and other adjuncts, return to a recirculation tank 19 through line 11. The separator may be as simple a device as a filter, or as complicated as a battery of tanks, washers, extractors, distillation columns, etc., suitable to each particular case. A by-pass line 50, connected to the system through a by-pass valve 52 is used to by-pass the separator 15, if so desired.

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At the vicinity of the upper end 14 of the reaction chamber 12, there is provided a gas outlet 23 leading to an outlet gas line 25.

There is also provided a liquid dispensing ring 44 on the wall 20 of the reaction chamber 12. The liquid dispensing ring 44 is connected to line 11', which provides liquid, preferably recovered. The ring 44 is adapted to distribute said liquid substantially uniformly on the inside surface 21 of the wall 20 in the form of a thick film or curtain 45.

The reaction chamber 12 is preferably adapted to withstand such temperatures and pressures, which are appropriate for the reaction conditions in the reaction chamber 12, and be suitable for the reactants and reaction products. Such materials and construction characteristics are well known to the art. For example, depending on the particular reaction, carbon steel, stainless steel, or Hastalloy may be required. In addition, the inside surface 21 may be protected by coatings or linings of vitreous or other materials.

Inside the reaction chamber 12, and preferably in the vicinity of the upper end 14, there is disposed an atomizer 26, preferably comprising a plurality of nozzles 27. The atomizer 26 is preferably of the airless type (does not need an atomizing gas for its operation). Airless atomizers are well known to the art. The atomizer 26 may be steady at a certain position of the reaction chamber 12, or it may be movable, preferably in an up/down mode. A driving mechanism 28, supporting the atomizer 26 is preferably connected to the reaction chamber 12 in the vicinity of the upper end 14. The driving mechanism 28 may be a hydraulic or pneumatic cylinder, or it may be of mechanical nature, such as one of the screw type, for example. It is mainly important that the driving mechanism 28 is adapted to move the atomizer 26 in a preferably up/down mode in a controllable manner, and without introducing leaks to the reaction chamber 12.

A gas inlet 34, preferably located in the vicinity of the lower end 16 of the reaction chamber 12, is connected to a gas inlet feed line 36, which provides the gas containing the second reactant.

In the vicinity of the lower part 16 of the reaction chamber 12, there is provided a sample collector 30, which is adapted to collect droplets of liquid and

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transfer them preferably as a miniature stream of liquid to a conversion detector (the word detector according to the present invention includes the meaning of monitor) 32 through sample line 33. The conversion detector 32 may also monitor the amount of first reactant and the amount of the intermediate oxidation product in the 5 recirculation tank 19 through a sample line 17. This information along with information on the nature and quantity of what is added in line 41, for example, can accurately determine the amounts of intermediate oxidation product and first reactant going to the atomizer 26.

10        A heat exchanger 38 is adapted to provide recirculated reactant mixture from the recirculation tank 19 to a replenishment receptacle 40, through inlet line 39. The replenishment receptacle 40 is also provided with fresh reactants, catalysts, solvents, and other adjuncts necessary for the reaction in each particular case through inlet line 41. The replenishment receptacle 40 may be a container 15 comprising temperature control (not shown) and a high pressure pump (not shown), which provides mixture made in the receptacle 40 to the nozzles 27 of the atomizer 26 through line 42 at a desired atomization temperature. Line 42 has a flexible, preferably coiled portion 43, so that it can follow any movements of the atomizer 26.

20        The device 10 also comprises a controller 35, preferably computerized, which is fed information regarding pre-coalescing transient conversion of reactants to intermediate oxidation product from conversion detector 32 through input line 31, and it controls heat exchanger 38 through output line 27, the drive mechanism 28 through output line 29, and the replenishment receptacle 40 through output line 37.

25        The monitor or detector 32 may be any instrument which is adaptable to detect the intermediate oxidation product or products. It may, for example, comprise a chromatography apparatus, a UV spectrograph, an IR spectrograph, a visible light spectrograph, a mass spectrometer, a NMR instrument, a conductivity monitor, an 30 ionization detector, a flame detector, any other suitable instrument, or a combination thereof.

In the case that the intermediate oxidation product is a non-volatile acid, it is

preferable that the monitor or detector 32 comprises a HPLC (High Pressure/Performance Liquid Chromatography instrument) in combination with a UV monitor. It is also preferable that the HPLC instrument has more than one columns, so that if the separation time in a column is longer than desired, consecutive 5 samples are introduced in different columns and a multiplicity of separations are conducted in parallel so that the interval between monitoring consecutive samples falls within desired limits. If it is desired to also analyze also non-polar organic moieties, it would be preferable to also include a gas chromatographic monitor or detector coupled with an appropriate monitor, such as an ionization monitor, for 10 example.

The method and the devices of the instant invention are particularly suitable for oxidation reactions of organic compounds, wherein the major portion of the oxidation product is an oxidation intermediate different than CO, CO<sub>2</sub>, or a mixture 15 thereof. One of the reasons why this is so, is that, due to the intricate criticalities of the present invention, the reaction rates, reaction homogeneity, yield, and other important properties are considerably improved, while in the absence of said criticalities complete oxidation to CO/CO<sub>2</sub> would take place. Actually, the same 20 conditions of atomization without said criticalities, are presently used in combustion engines of automobiles and other devices, to substantially completely oxidize (combust or burn in other words) organic compounds such as gasoline to a mixture of CO/CO<sub>2</sub>.

In contrast, according to the present invention, if for example, the first 25 reactant is cyclohexane, the major portion of the oxidation product may be substantially cyclohexanol, cyclohexanone, cyclohexylhydroperoxide, caprolactone, adipic acid, the like, and mixtures thereof. Organic acids are preferable oxidation products.

30 The operation of this, as well as the other embodiments of the instant invention, will be discussed for any non-destructive oxidation encompassed by the claims, and at the same time it will be exemplified, by using cyclohexane as a first reactant, oxygen as the oxidant in the gas, and adipic acid as the intermediate

oxidation product. The term "intermediate oxidation product", as aforementioned, signifies that the oxidation stops before substantially oxidizing the first reactant to carbon monoxide, carbon dioxide, or mixtures thereof.

5 In operation of this embodiment, a first liquid containing the first reactant, cyclohexane for example, enters the reaction chamber 12 through line 42 in a manner that it is atomized by the atomizer 26 and nozzles 27, in a manner to form a plurality of droplets 48. The first liquid enters the atomizer at a desired atomization temperature, which in the case of cyclohexane is preferably in the range of 50-150°  
10 C, more preferably in the range of 80 - 130° C, and even more preferably in the range of 90 - 120°. Atomization temperature of the first liquid is the temperature of the liquid just before it is atomized. The temperature of the just formed droplets may be the same or different than the atomization temperature. In the case of cyclohexane, the first liquid also preferably contains a solvent, such as acetic acid,  
15 for example, a catalyst, such as a cobalt compound, soluble in the first liquid, for example, and an initiator, such as cyclohexanone, methylethylketone, acetaldehyde, the like, and mixtures thereof, for example. The pressure in the case of oxidation of cyclohexane to adipic acid should preferably be high enough to maintain the cyclohexane, solvents, initiators, etc., substantially in the liquid state. Although  
20 pressures even in excess of 1,000 psia are possible, pressures in the range of 100 to 400 psia are preferable, and pressures in the range of 150 to 300 psia more preferable.

The atomizer 26 is initially preferably placed, by the drive mechanism 28, at a  
25 low position close to the lower end 16 of the reaction chamber 12 (although in Figure 1 the atomizer 26 happens to have a position in the vicinity of the upper end 14 of the reaction chamber 14), at a distance from a mass of a second liquid 54, which has a second surface 56, and which is collected and disposed of at the lower end 16 of the reaction chamber 12 through liquid outlet 22. The second liquid is a combination  
30 of coalesced droplets 48 and liquid from the thick film or curtain 45. The distance between the nozzle of the atomizer which is closest to the surface 56 of the mass 54, and the surface 56 of the mass of the second liquid 54 is defined as the atomization distance. If the second liquid 54 has been removed completely from the

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reaction chamber 12, the atomization distance is defined as the distance between the nozzle of the atomizer which is closest to the point where the liquid outlet 22 meets the reaction chamber, and that point. The atomization distance at the beginning of the operation is preferably about one third to one fourth of the maximum atomization distance. The maximum atomization distance is the atomization distance when the atomizer is as far away from the surface 56 of the second liquid mass 54 as the design of the device 10 and the atomizer 26 allows. The atomizer has the maximum atomization distance in Figure 1.

10 At the same time that the first liquid is being atomized, a gas containing the oxidant, preferably oxygen in the case of cyclohexane, enters the chamber 12 through the gas inlet feed line 36, in the vicinity of the lower end 16 of the chamber 12. The gas, in addition to the oxidant, may also contain rather inert gases, such as nitrogen and/or carbon dioxide for example. Off gases mixed with vapors of 15 reactants, solvents, mist, and the like exit the reaction chamber through outlet gas line 25 and are treated as it will exemplified at a later section.

As the droplets fall in a downwardly direction from the atomizer 26, they start reacting with the oxidant, which is oxygen for example. The second liquid 54 is 20 removed, preferably continuously, through the liquid outlet 22, and it is pumped (pump not shown) through liquid outlet line 24 to a separator 15, where the intermediate oxidation product, adipic acid for example, is separated from the liquids by techniques well known to the art. In some occasions, other by-products of the oxidation may also be removed in the separator, if so desired. Reactants, solvents, 25 catalysts, and the like, return through line 11 to the recirculation tank 19.

Part of the second liquid, after the above product and/or by-product removal treatment, may be directed to the liquid dispensing ring 44, through line 11', if so desired, where it is dispensed in the form of the thick film or liquid curtain 45, and covers the inside surface 21 of the wall 20 of the reaction chamber 12. The 30 temperature of this film, when it is dispensed from the dispensing ring 44 is arranged to be lower than the atomization temperature. In the case of cyclohexane to adipic acid, for example, it is preferably in the range of 20° to 80° C, and more preferably in the range of 20° to 40° C. At this lower temperature, no appreciable reaction takes

place, and any droplets coalescing onto the film do not have much effect to the process. Any solid products which are insoluble in the droplets are washed down by the liquid curtain 45, and they form the second liquid 54 along with the coalesced droplets 48, as already mentioned. Thus, no sticking of solids takes place on the 5 inside surface 21 of the wall 20. It should be noted that unrecycled liquids, which might be just solvents, or just reactants with or without catalysts or other adjuncts, or other liquids, or any combination thereof, may replace or supplement the recycled liquid coming from line 11'. If so desired, the second liquid transported in line 24 may by-pass the separator 15 through by-pass valve 52 and by-pass line 50 either 10 partially or totally. This option may be utilized, especially at the beginning of the operation, if the pre-coalescing transient conversion is under a desired pre-coalescing transient conversion level.

Measures are taken for the level or surface 56 of second liquid 54 not to 15 move over the point at which the sample collector 30 is positioned, to prevent flooding of the sample collector 30 with second liquid 54, which will produce false sampling. Monitoring a liquid level is very well known to the art and may be conducted with any suitable type of "liquid level monitor", available in the market. The liquid level monitor is then arranged to control the supply of liquids entering the 20 reaction chamber 12 as curtain 45 though line 11', as droplets through the atomizer 26, or exiting the reaction chamber 12 as second liquid 54 through outlet liquid line 24, or any combination thereof, so as to keep the level or surface 56 of the second liquid mass 54 within desired limits under the sample collector 30. Such an arrangement is very simple, and it is not shown in Figure 1 for clarity purposes. 25 Higher supply of liquids through line 11' and the atomizer will cause the level of surface 56 to be raised, while lower supply will have the opposite effect. Similarly, higher removal rate through line 24 will cause the level of or surface 56 to be lowered, while lower removal rate will have the opposite effect.

30 A part of the droplets 48 fall into the sample collector 30, just above the surface 56 of the second liquid mass 56, from where, they are directed to the conversion detector or monitor 32, to be analyzed regarding pre-coalescing transient conversion. If solids are present in the droplets, care should be taken to prevent

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clogging of liquid transporting lines by use of appropriate dilution, and the like. As aforementioned, in the case of adipic or other acid formation, it is preferable that the monitor 32 comprises a chromatography apparatus, which more preferably is a High Performance (or Pressure) Liquid Chromatography apparatus (HPLC). This apparatus, as also mentioned earlier, may preferably have an adequate number of columns, so that it is capable of making a respective number of overlapping determinations of the intermediate oxidation product present in the droplets just before they coalesce into the mass of the second liquid 54, so that the pre-coalescing transient conversion of the first reactant to intermediate reaction product is checked as frequently as desired in each particular case. If the column, for example, separates the intermediate oxidation product in 8 minutes, and the desired interval between determinations is 2 minutes in a particular case, four columns are needed.

15 Sampling of the liquid in the recirculation tank 19 or at a point just before it is atomized, may be desirable, and it may be carried out in the same detector 32, through line 17 or other lines (not shown) respectively, or by means of another detector (not shown).

20 The information obtained in the conversion detector or monitor 32 is fed to computerized controller 35 through its input line 31, where it is processed by well known to the art techniques. The controller 35 controls the heat exchanger 38 through its output line 46, which along with the temperature of the liquids provided through line 41, determines the temperature in the replenishment receptacle 40, 25 which temperature is substantially the same as the atomization temperature for all practical purposes. Controller 35 through its output line 37, controls the feed rate of first liquid through line 42. In addition, controller 35, through its output line 29, controls the drive mechanism 28.

30 If the pre-coalescing transient conversion is above a range called according to this invention "pre-coalescing transient conversion range" because it represents the pre-coalescing transient conversion just before the droplets coalesce on to the second liquid 54, the drive mechanism 28 is ordered by the controller 35 to lower the

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level of atomizer in a manner that the atomization distance, as defined above, decreases. The change of atomization distance is preferably conducted in increments, preferably in the range of 10 to 50% of the atomization distance at the particular time, and more preferably in the range of 10 to 30%. However, other 5 ranges may be more appropriate, depending on the particular conditions, materials, previous determination, and the like. For example, if a 10% decrease in atomization distance is found not to have an appreciable result, the following increment may be 30%, for example. On the other hand, if a 10% decrease in the atomization distance results in an overwhelming change in pre-coalescing transient conversion, the next 10 increment may be 5%, for example, until the conversion falls within the desirable range, and preferably in the most desirable range. It should be pointed out again, however, that the desirable ranges may change, depending on materials, conditions, etc. The distance between the sample collector 30 and the level or surface 56 of the second liquid mass 54 is preferably in the range of 5 - 10% of the maximum 15 atomization distance

After the pre-coalescing transient conversion is found to be within the most desired, it continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range. Continuous monitoring 20 and control are highly desirable, since the conditions in the reaction chamber may vary, causing changes in the pre-coalescing transient conversion values.

The preferable predetermined pre-coalescing transient conversion range is 0.05% to 80%

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It should be noted that if the reaction is very slow for some reason, or if so desired, partial or total recirculation (not shown) directly from line 24 to line 42 is advisable, with or without additional feeding of line 42 from replenishment receptacle 40.

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The pre-coalescing transient conversion can be also calculated or measured from samples of the second liquid, after taking into account any factors which change the concentration of the reaction product in the droplets.

In another embodiment of the present invention, better shown in Figure 1A, there is also provided a thermocouple 60a adapted to monitor the pre-coalescing temperature of the droplets.

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The controller 35 in this case is fed information regarding the pre-coalescing temperature through input line 60a' and the pre-coalescing transient conversion of reactants to intermediate oxidation product from conversion detector 32 through input line 31. In turn, the controller 35, as in the previous case, controls heat exchanger 38 through output line 46, the drive mechanism 28 through output line 29, and the replenishment receptacle 40 through output line 37, and feed rate in line 42.

In operation of this embodiment, a part of the droplets 48 fall onto 15 thermocouple 60a, which in turn feeds the pre-coalescing temperature information to the controller 35 through input line 60a'. At the same time part of the droplets also fall into the sample collector 30, just above the surface 56 of the second liquid mass 56, from where, they are directed to the conversion detector or monitor 32, to be analyzed regarding pre-coalescing transient conversion. The information obtained in 20 the conversion detector or monitor 32 is fed to computerized controller 35 through its input line 31, where it is processed by well known to the art techniques along with information received through line 60a' regarding the pre-coalescing temperature of the droplets.

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If the pre-coalescing temperature attains precedence over the pre-coalescing transient conversion, the controller 35 makes decisions based on the pre-coalescing temperature first. If the pre-coalescing temperature is above the pre-coalescing temperature range, the drive mechanism 28 is ordered by the controller 35 to lower the level of atomizer in a manner that the atomization distance, as 30 defined above, decreases. The change of atomization distance is preferably conducted in increments, preferably in the range of 10 to 50% of the atomization distance at the particular time, and more preferably in the range of 10 to 30%. However, other ranges may be more appropriate, depending on the particular

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conditions, materials, previous determination, and the like. For example, if a 10% decrease in atomization distance is found not to have an appreciable result, the following increment may be 30%, for example. On the other hand, if a 10% decrease in the atomization distance results in an overwhelming change in pre-coalescing temperature, the next increment may be 5%, for example, until the pre-coalescing temperature falls within the desirable range, preferably in the most desirable range, and even more preferably if it attains a value in the vicinity of its most preferred set value.

10 It should be pointed out again, however, that the desirable ranges may change, depending on materials, conditions, etc. The distance between the thermocouple 60a and the level or surface 56 of the second liquid mass 54 is preferably in the range of 5 - 10% of the maximum atomization distance.

15 In the case of oxidation of cyclohexane to adipic acid, for example, the preferred pre-coalescing temperature range is 50 - 150° C, more preferably 80 - 130° C, and even more preferably 90 - 120° C.

20 After the pre-coalescing temperature is found to be within the most desired range (90 - 120° C, for example, in the case of cyclohexane to adipic acid under certain conditions), it continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range (about 105° C, for example, which is the most desired value). Continuous monitoring and control are, of course, highly desirable, since the conditions in the reaction 25 chamber may vary, causing changes in the pre-coalescing temperature.

30 The above operation is conducted for as long as the pre-coalescing transient conversion is closer to its most preferable set value than the pre-coalescing temperature. When at some point, the pre-coalescing transient conversion is found to be further away to its respective most preferred value than the pre-coalescing temperature, or if it is driven to fall outside its respective predetermined range, then the pre-coalescing transient conversion takes precedence, and an operation as described in the previous embodiment is conducted.

In another embodiment of the present invention, better shown in Figure 2, the reaction chamber 112 is provided with an atomizer 126 in the vicinity of its upper end 114, and a sample collector 130 positioned in the vicinity of its lower end 116. There 5 is also provided a supplementary heat exchanger 158 and a temperature measuring device, such as a thermocouple 160, for example. The liquid dispensing ring 144 is shown at the beginning of the conical portion of the reactor, but it may take any position on the wall of the reactor, or it may be omitted all together. The same holds true for all embodiments of the present invention. The sample collector 130 is 10 connected to the conversion monitor or detector 132 through line 133 for providing samples of droplets 148 trapped in the collector just (and coalesced, of course in the collector) before they coalesce onto the second liquid mass 154. The thermocouple 160 and the conversion monitor or detector 132 are connected, preferably electrically, to the controller 135 through input lines 160' and 131, respectively. In 15 turn, the controller 135 is connected, preferably electrically, to the supplemental heat exchanger 158 through output line 158' in order to control said supplemental heat exchanger 158. For purposes of clarity, basically only the elements of the device 110, which illustrate this embodiment and its operation, are shown.

20 In operation of this embodiment, the first liquid containing the first reactant, cyclohexane for example, enters the reaction chamber 112 through line 142 in a manner that it is atomized by the atomizer 126, in a manner to form a plurality of droplets 148.

25 At the same time that the first liquid is being atomized, a gas containing the oxidant, preferably oxygen in the case of cyclohexane, enters the chamber 112 through the gas inlet feed line 136, in the vicinity of the lower end 116 of the chamber 112. The gas, in addition to the oxidant, may also contain rather inert gases, such as nitrogen and/or carbon dioxide for example. Off gases mixed with 30 vapors of reactants, solvents, mist, and the like exit the reaction chamber through outlet gas line 125 and are treated as it will exemplified at a later section.

As before, the droplets start reacting with the oxidant, which is oxygen for

example. A part of the droplets 148 fall into the sample collector 130, from where, they are directed to the conversion detector or monitor 132, to be analyzed regarding pre-coalescing transient conversion.

5 The information obtained in the conversion detector or monitor 132 is fed to computerized controller 135 through its input line 131, where it is processed by well known to the art techniques. Also, the atomization temperature from thermocouple 160 is fed to the computerized controller 135. The controller 135 controls the heat exchanger 158 through its output line 158'.

10 If the pre-coalescing transient conversion is above the pre-coalescing transient conversion range, as earlier defined, the heat exchanger is ordered by the controller 135 to lower the atomization temperature, monitored by thermocouple 160. Similarly, if the pre-coalescing transient conversion is under the "pre-coalescing 15 transient conversion range", according to this invention, the heat exchanger is ordered by the controller 35 to increase the atomization temperature. The upper and lower limits of the atomization temperature depend on the reactants, conditions of the reaction, and the like. For example, in the case of oxidation of cyclohexane to adipic acid, the upper limit should preferably be maintained not higher than 170° C, 20 and more preferably not higher than 150° C, while the lower limit should preferably maintained not lower than 50° C, and more preferably not lower than 70° C.

25 The change of atomization temperature is preferably conducted in increments, preferably in the range of 5 to 10% of the atomization temperature at the particular time.

After the pre-coalescing transient conversion is found to be within the most desired range, it continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range. As in the 30 previous embodiments continuous monitoring and control are highly preferable, since the conditions in the reaction chamber may vary, causing changes in the pre-coalescing transient conversion values.

In a different embodiment of the present invention, better shown in Figure 2A, a thermocouple 160a is disposed at the lower end 116 of the reaction chamber 112 for monitoring the pre-coalescing temperature. A shield 190, positioned under the thermocouple 160a, is to protect the thermocouple 160a from temperature changes due to drafts of ascending gases. Another thermocouple 160 is disposed within the atomizer 126 for measuring the atomization temperature. Both thermocouples 160 and 160a are connected to the controller 135 through input lines 160' and 160a', respectively. In turn, the controller 135 is connected, preferably electrically, to the supplemental heat exchanger 158 through output line 158' in order to control said supplemental heat exchanger 158. For purposes of clarity, basically only the elements of the device 110, which illustrate this embodiment and its operation, are shown.

In operation of this embodiment, the first liquid containing the first reactant, 15 cyclohexane for example, enters the reaction chamber 112 through line 142 in a manner that it is atomized by the atomizer 126 to form a plurality of droplets 148.

20 A part of the droplets 148 fall onto the thermocouple 160a, which in turn the pre-coalescing temperature information to the computerized controller 135 through its input line 160a', where it is processed by well known to the art techniques. Also, the atomization temperature from thermocouple 160 is fed to the computerized controller 135 through input line 160'. The controller 135 controls the heat exchanger 158 through its output line 158'.

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If the pre-coalescing temperature takes precedence and is above the pre-coalescing temperature range, as earlier defined, the heat exchanger is ordered by the controller 135 to lower the atomization temperature, monitored by thermocouple 160. Similarly, if the pre-coalescing temperature is under the pre-coalescing 30 temperature range, according to this invention, the heat exchanger is ordered by the controller 35 to increase the atomization temperature. The upper and lower limits of the atomization temperature depend on the reactants, conditions of the reaction, and the like. For example, in the case of oxidation of cyclohexane to adipic acid, the

upper limit should preferably be maintained not higher than 170° C, and more preferably not higher than 150° C, while the lower limit should preferably be maintained not lower than 50° C, and more preferably not lower than 70° C.

5 The change of atomization temperature is preferably conducted in increments, preferably in the range of 5 to 10% of the atomization temperature at the particular time.

After the pre-coalescing temperature, is found to be within the most desired 10 range (90 - 120° C, for example, in the case of cyclohexane to adipic acid for example under certain conditions), it continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle or most preferred set value of said most desired range (about 115° C, for example). As in the previous 15 embodiment, continuous monitoring and control are highly preferable, since the conditions in the reaction chamber may vary, causing changes in the transient conversion values.

Changes in atomization temperature necessarily cause changes in the transient temperature difference, so that the transient temperature difference is a 20 moving target. This is of no concern, however, especially to the recent computerized controllers, well known to the art.

If and when the transient temperature difference falls further away from its most desired value than the pre-coalescing temperature does, then the transient 25 temperature difference takes precedence. If it is at a higher value than its most desired set value, the heat exchanger is ordered by the controller 135 to lower the atomization temperature, monitored by thermocouple 160. Similarly, if the transient temperature difference is at a lower value than its desired set value, according to this invention, the heat exchanger is ordered by the controller 35 to increase the 30 atomization temperature. The upper and lower limits of the atomization temperature depend on the reactants, conditions of the reaction, and the like. For example, in the case of oxidation of cyclohexane to adipic acid, the upper limit should preferably be maintained not higher than 170° C, and more preferably not higher than 150° C,

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while the lower limit should preferably maintained not lower than 50° C, and more preferably not lower than 70° C.

The change of atomization temperature is preferably conducted in  
5 increments, preferably in the range of 5 to 10% of the atomization temperature at  
the particular time.

After the transient temperature difference is found to be within the most  
desired range, it continues to be monitored with a goal in most cases to stay  
10 somewhere in the vicinity of the middle or most preferred set value of said most  
desired range. As in the previous embodiment, continuous monitoring and control  
are highly preferable, since the conditions in the reaction chamber may vary,  
causing changes in the transient temperature difference values.

15 In a different embodiment of the present invention, better shown in Figure 3,  
the reaction chamber 212 is provided with an atomizer 226 in the vicinity of its upper  
end 214, and a sample collector 230 positioned in the vicinity of its lower end 216.  
There is also provided a pressurizing pump 263 communicating with the reaction  
chamber 212 through line 236, a flow meter 266 in the line 236, a gas mixing valve  
20 268 connected on one side to an oxidant feed line 247 and an other gas line 249,  
and a pressure measuring device, such as a pressure gauge 262, for example for  
monitoring the pressure inside the reaction chamber 212. The liquid dispensing ring  
244 is shown at about the middle of the wall of the reaction chamber 212, but it may  
take any position on the wall, or it may be omitted all together. The sample collector  
25 230 is connected to the conversion monitor or detector 232 through line 233 for  
providing samples of droplets 248 trapped in the collector, just (and coalesced, of  
course, in the collector) before they coalesce onto the second liquid mass 254. The  
pressure gauge 262, the flow meter 266, and the conversion monitor or detector 232  
are connected, preferably electrically, to the controller 235 through input lines 262',  
30 266', and 231, respectively. In turn, the controller 235 is connected, preferably  
electrically, to the pressurizing pump 263 through output line 263', to the gas mixing  
valve 268 through output line 268', and to valve 264 through output line 264'. The  
controller 235 is adapted to control the pressurized pump 263, the gas mixing valve

268, and the valve 264. For purposes of clarity, basically only the elements of the device 210, which illustrate this embodiment and its operation, are shown.

In operation of this embodiment, the valve 264 is initially closed or turned to the off position. The gas mixing valve 268 is regulated to deliver a desired ratio of oxidant to inert gas (which ratio determines the content of oxidant in the total gas, defined earlier as the second content) to the pressurizing pump 263, obtained from lines 247 and 249, respectively. The pressurizing pump is then turned on until the desired pressure is attained in the reaction chamber 212. In sequence, with the pressurizing pump still on, the valve 264 is opened to such a degree that the desired pressure is maintained in the reaction chamber. If the flow rate (second flow rate being the flow rate of the gas, as defined above), as measured from the flowmeter 266, is too high, the pump is turned to a lower speed and the valve 264 is turned to a less open position in a manner to maintain the desired pressure at a lower second flow rate. This is continued until both the pressure and second flow rate attain desired values. If the second flow rate, as measured from the flowmeter 266, is too low, the pump is turned to a higher speed and/or the valve 264 is turned to a more open position in a manner to maintain the desired pressure at a higher second flow rate. This is continued until both the pressure and the second flow rate attain desired values.

After both pressure and the second flow rate have attained their initial desired values, the first liquid, after having been heated to the atomization temperature as described before, which liquid contains the first reactant, cyclohexane for example, enters the reaction chamber 212 through line 242 in a manner that it is atomized by the atomizer 226, and forms a plurality of droplets 248.

At the same time that the first liquid is being atomized, the mixed gas containing the oxidant, preferably oxygen in the case of cyclohexane, enters the chamber 212 through the gas inlet feed line 236, in the vicinity of the lower end 216 of the reaction chamber 212. The desired ratio of the gases (defining the second content as discussed earlier) depends on the reaction and conditions, and it may have any value suitable for the circumstances. In most cases the preferable oxidant

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is oxygen and the other gas is an inert gas, such as nitrogen or carbon dioxide, for example. Off gases mixed with vapors of reactants, solvents, mist, and the like exit the reaction chamber 212 through outlet gas line 225, and are treated as it will be exemplified at a later section.

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As the droplets fall in a downwardly direction from the atomizer 226, they start reacting with the oxidant, which is oxygen for example. The second liquid 254 is removed, preferably continuously, through the liquid outlet line 224 as in the previous embodiments.

10

Part of the second liquid, after removal of the oxidation product and/or by-products, in the separator 15 shown in Figure 1, may be directed to the liquid dispensing ring 244, through line 211', if so desired, where it is dispensed in the form the thick film or liquid curtain 245, as in the previous embodiments.

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A part of the droplets 248 fall into the sample collector 230, from where, they are directed to the conversion detector or monitor 232, to be analyzed regarding pre-coalescing transient conversion.

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The information obtained in the pre-coalescing transient conversion detector or monitor 232 is fed to computerized controller 235 through its input line 231, where it is processed by well known to the art techniques. Also, the pressure within the reaction chamber from gauge 262, and the flow rate of gases (second flow rate) through line 236 measured by the flow meter 266 are fed to the computerized controller 235 through input lines 262' and 266', respectively. As aforementioned, the controller 235 controls the pressurizing pump 263 through its output line 263', valve 264 through its output line 264', and gas mixing valve 268 through its output line 268'.

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Controlling the pressurizing pump means that the controller is adapted to change the pressure and flow output of the pressurizing pump based on data received from input lines 231, 266', and 262', said data being processed according to a desired program. Controlling the valve 264 means that it is adapted to

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open/close said valve 264 to a desired degree based on data received from input lines 231, 266', and 262', said data being processed according to a desired program. Controlling the gas mixing valve 268 means that it is adapted to regulate said valve 268 in a manner to feed the pressurizing pump 263 with a mixture of 5 oxidant provided by line 247 and other (such as inert for example) gas provided by line 249, so that the mixture has a desired weight ratio, based on data received from input lines 231, 266', and 262', said data being processed according to a desired program. Programming computerized controllers is well known to the art.

10 As it can be seen in Figure 3, two elements which can determine the pressure inside the reaction chamber 212, as well as the second flow rate in this embodiment, are the pressurizing pump 263 and the valve 264. Other elements in line 225, such as condensers (not shown), gas recirculation assemblies (not shown), and the like for example, may also influence the pressure, mostly temporarily, but 15 they have been omitted from Figure 3 for purposes of clarity. They will be discussed at a later section. The more gas the pressurizing pump dispenses to the reaction chamber 212, and the more closed the valve 264 is the higher the pressure inside the reaction chamber. The less gas the pressurizing pump dispenses to the reaction chamber 212, and the more open the valve 264 the lower the pressure inside the 20 reaction chamber. Of course, the flow or delivery rate of gas by the pressurizing pump 263 and the degree of opening of the valve 264 have to be coordinated in order to achieve a desired pressure inside the reaction chamber.

25 The data received in the computerized controller 235 may be used after being processed in a number of ways, or combinations thereof, to control the pre-coalescing transient conversion and maintain it within the pre-coalescing transient conversion range.

30 One way is to vary the flow rate of the gas (second flow rate) entering the reaction chamber 212 through line 236. If the pre-coalescing transient conversion, as measured in the pre-coalescing transient conversion monitor or detector 232 has a higher value than the desired pre-coalescing transient conversion range, the computerized controller 235 orders the pressurizing pump to decrease the second

flow rate as measured by the flowmeter 266. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more closed or restricted position so that the pressure inside the reaction chamber 212, as measured by the pressure gauge 262, tends to remain within the desired range. This is continued until the 5 second flow rate has attained a newly desired value, and pressure is within the desired range. If the pre-coalescing transient conversion, as measured in the conversion monitor or detector 232 has a lower value than the desired pre-coalescing transient conversion range, the computerized controller 235 orders the pressurizing pump to increase the second flow rate as measured by the flowmeter 10 266. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more open position, so that the pressure inside the reaction chamber 212, as measured by the pressure gauge 262, tends to remain within the desired range. This is continued until the second flow rate has attained a newly desired value and the pressure is within the desired range. The second flow rate changes (increase or 15 decrease) from one value to a newly desired value should preferably be in increments, preferably in the range of 5-20% and more preferably in the range of 5-10%. Also, changes should preferably be ordered by the computerized controller in time intervals long enough to contain at least one new pre-coalescing transient conversion measurement in the conversion monitor or detector 232.

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If the pre-coalescing transient conversion under the newly attained second flow rate does not fall within the predetermined pre-coalescing transient conversion range, the same process is repeated until the pre-coalescing transient conversion finally falls within the desired pre-coalescing transient conversion range.

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Another way is to vary the ratio of the oxidant to the inert or other gas entering the reaction chamber 212 through line 236. If the pre-coalescing transient conversion, as measured in the conversion monitor or detector 232 has a higher value than the desired pre-coalescing transient conversion range, the computerized 30 controller 235 orders the gas mixing valve 268 to decrease said ratio. If the pre-coalescing transient conversion, as measured in the conversion monitor or detector 232 has a lower value than the desired pre-coalescing transient conversion range, the computerized controller 235 orders the gas mixing valve 268 to increase said

ratio. The ratio changes (increase or decrease) from one value to a newly desired value should preferably be in increments, preferably in the range of 5-20% and more preferably in the range of 5-10%. Also, changes should preferably be ordered by the computerized controller in time intervals long enough to contain at least one new 5 pre-coalescing transient conversion measurement in the conversion monitor or detector 232.

Still a different way is to vary the pressure of the gas in the reaction chamber 212 in many occasions, where increase in pressure increases reactivity to a 10 substantial degree. If the pre-coalescing transient conversion, as measured in the pre-coalescing transient conversion monitor or detector 232 has a higher value than the desired pre-coalescing transient conversion range, the computerized controller 235 orders the pressurizing pump to slow down. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more open position so that the 15 second flow rate, as measured by the flow meter 266, tends to remain within the desired range. This is continued until the pressure has attained a newly desired value, and the second flow rate is within the desired range. If the pre-coalescing transient conversion, as measured in the conversion monitor or detector 232 has a lower value than the desired pre-coalescing transient conversion range, the 20 computerized controller 235 orders the pressurizing pump to speed up. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more closed position so that the second flow rate, as measured by the flow meter 266, tends to remain within the desired range. This is continued until the pressure has attained a 25 newly desired value, and the second flow rate is within the desired range. The pressure changes (increase or decrease) from one value to a newly desired value should preferably be in increments, preferably in the range of 2-20% and more preferably in the range of 5-10%. Also, changes should preferably be ordered by the computerized controller in time intervals long enough to contain at least one new pre-coalescing transient conversion measurement in the conversion monitor or 30 detector 232.

If the pre-coalescing transient conversion under the newly attained pressure does not fall within the predetermined pre-coalescing transient conversion range, the

same process is repeated until the pre-coalescing transient conversion finally falls within the desired pre-coalescing transient conversion range.

In a different embodiment of the present invention, better shown in Figure 5 3A, the reaction chamber 212 is provided with an atomizer 226, having a thermocouple 260, in the vicinity of its upper end 214, and a thermocouple 260a in the vicinity of the lower end 216 of the reaction chamber 212. The thermocouple 260a is connected to the controller 235 through input line 260a' for providing the temperature of droplets 248 before they coalesce onto the second liquid mass 254.

10 The pressure gauge 262, the flow meter 266, the thermocouple 260, and the thermocouple 260a are connected, preferably electrically, to the controller 235 through input lines 262', 266', 260', and 260a', respectively. As in the previous embodiment, the controller 235 is connected, preferably electrically, to the pressurizing pump 263 through output line 263', to the gas mixing valve 268 through 15 output line 268', and to valve 264 through output line 264'. The controller 235 is adapted to control the pressurized pump 263, the gas mixing valve 268, and the valve 264.

20 The operation of this embodiment is very similar to the operation of the previous embodiment, with the difference that the determinant in this case is the transient temperature difference or the pre-coalescing temperature, or a combination thereof.

25 A part of the droplets 248 fall onto thermocouple 260a, which measures their temperature in the form of an electrical signal, which is fed to computerized controller 235 through its input line 260a', where it is processed by well known to the art techniques. In addition, the atomization temperature in the atomizer 226 is measured by thermocouple 260, in the form of another electrical signal, which is fed to computerized controller 235 through its input line 260', where it is processed 30 along with the rest of the information that the controller 235 receives.

The data received in the computerized controller 235 may be used after being processed in a number of ways, or combinations thereof, to control the pre-

coalescing temperature and/or the transient temperature difference, and maintain them within their respective predetermined ranges.

One way is to vary the flow rate of the gas (second flow rate) entering the

5 reaction chamber 212 through line 236. If the prevailing determinant, has a higher value than the desired respective predetermined range, the computerized controller 235 orders the pressurizing pump to decrease the second flow rate as measured by the flowmeter 266. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more closed or restricted position so that the pressure inside the

10 reaction chamber 212, as measured by the pressure gauge 262, tends to remain within the desired range. This is continued until the second flow rate has attained a newly desired value, and pressure is within the desired range. If the prevailing determinant has a lower value than the respective predetermined range, the computerized controller 235 orders the pressurizing pump to increase the second

15 flow rate as measured by the flowmeter 266. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more open position, so that the pressure inside the reaction chamber 212, as measured by the pressure gauge 262, tends to remain within the desired range. This is continued until the second flow rate has attained a newly desired value and the pressure is within the desired range.

20 The second flow rate changes (increase or decrease) from one value to a newly desired value should preferably be in increments, preferably in the range of 5-20% and more preferably in the range of 5-10%. Also, changes should preferably be ordered by the computerized controller in time intervals long enough to allow for adequate equilibrium for prevention of over-shooting.

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If the prevailing determinant under the newly attained second flow rate does not fall within the respective predetermined range, the same process is repeated until the prevailing determinant finally falls within the desired predetermined range.

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Another way is to vary the ratio of the oxidant to the inert or other gas entering the reaction chamber 212 through line 236. If the prevailing determinant has a higher value than the desired respective predetermined range, the computerized controller 235 orders the gas mixing valve 268 to decrease said ratio.

If the prevailing determinant has a lower value than the desired respective predetermined range, the computerized controller 235 orders the gas mixing valve 268 to increase said ratio. The ratio changes (increase or decrease) from one value to a newly desired value should preferably be in increments, preferably in the range 5 of 5-20% and more preferably in the range of 5-10%. Also, changes should preferably be ordered by the computerized controller in time intervals long enough to allow for adequate equilibrium for prevention of over-shooting.

Still a different way is to vary the pressure of the gas in the reaction chamber 10 212 in many occasions, where increase in pressure increases reactivity to a substantial degree. If the prevailing determinant has a higher value than the desired respective predetermined range, the computerized controller 235 orders the pressurizing pump to slow down. At the same time, the valve 264 is ordered by controller 235 to attain a somewhat more open position so that the second flow rate, 15 as measured by the flow meter 266, tends to remain within the desired range. This is continued until the pressure has attained a newly desired value, and the second flow rate is within the desired range. If the prevailing determinant has a lower value than the desired pre-coalescing transient conversion range, the computerized controller 235 orders the pressurizing pump to speed up. At the same time, the 20 valve 264 is ordered by controller 235 to attain a somewhat more closed position so that the second flow rate, as measured by the flow meter 266, tends to remain within the desired range. This is continued until the pressure has attained a newly desired value, and the second flow rate is within the desired range. The pressure changes (increase or decrease) from one value to a newly desired value should 25 preferably be in increments, preferably in the range of 2-20% and more preferably in the range of 5-10% of the pressure at that time. Also, changes should preferably be ordered by the computerized controller in time intervals long enough to obtain adequate equilibrium for prevention of over-shooting.

30 If the prevailing determinant under the newly attained pressure does not fall within the desired respective predetermined, the same process is repeated until the prevailing determinant finally falls within the desired range.

The preferable program rules and overriding program rules described earlier, apply in this and the other embodiments.

In another embodiment of the present invention, better shown in Figure 4, 5 the reaction chamber 312 is provided with an atomizer 326 in the vicinity of its upper end 314, and a sample collector 330 positioned in the vicinity of its lower end 316. There is also provided a reactant mixing valve 369, which is adapted to mix first reactant from line 370 and other liquids from line 371 in order to produce the first liquid in line 342 having a first content of first reactant. The sample collector 330 is 10 connected to the conversion monitor or detector 332 through sample line 333 for providing samples of droplets 348 trapped in the collector just (and coalesced, of course in the collector) before they coalesce onto the second liquid mass 354. The conversion monitor or detector 332 is connected, preferably electrically, to the controller 335 through input line 331 for transferring pre-coalescing transient 15 conversion information. In turn, the controller 335 is connected, preferably electrically, to the reactant mixing valve 369 through output line 369' in order to control said reactant mixing valve 369. For purposes of clarity, basically only the elements of the device 310, which illustrate this embodiment and its operation, are shown.

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In operation of this embodiment, first reactant from line 370 and other liquids from line 371 are mixed in proportions regulated by the reactant mixing valve 369, in order to produce the first liquid in line 342 so that said first liquid has a first content of first reactant. The liquids from line 371 may contain solvents, catalysts, promoters, 25 initiators, recycled ingredients, first reactant, and the like. If the liquids from line 371 contain first reactant, the content of these liquids in first reactant has to be taken into account in the determination of the first content of first reactant in line 342, so that the reactant mixing valve 369 allows accordingly less first reactant from line 370. The first liquid containing the first reactant, cyclohexane for example, in a first content, 30 enters the reaction chamber 312 through line 342 in a manner that it is atomized by the atomizer 326, and forms a plurality of droplets 348.

As the droplets fall in a downwardly direction from the atomizer 326, they

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start reacting with the oxidant, which is oxygen for example. The second liquid 354 is removed, preferably continuously, through the liquid outlet line 324 as in the previous embodiments.

5 A part of the droplets 348 fall into the sample collector 330, from where, they are directed to the conversion detector or monitor 332, to be analyzed regarding pre-coalescing transient conversion.

10 The information obtained in the conversion detector or monitor 332 is fed to computerized controller 335 through its input line 331, where it is processed by well known to the art techniques. The controller 335 controls the reactant mixing valve through its output line 369'.

15 If the pre-coalescing transient conversion is above the pre-coalescing transient conversion range, as earlier defined, the reactant mixing valve 369 is ordered by the controller 335 to increase the first content by increasing the ratio of the first reactant from line 370 to liquids from line 371. Similarly, if the pre-coalescing transient conversion is under the "pre-coalescing transient conversion range", according to this invention, the reactant mixing valve 369 is ordered by the controller 20 335 to decrease the first content by decreasing the ratio of the first reactant from line 370 to liquids from line 371.

25 The change of first content is preferably conducted in increments, preferably in the range of 5 to 10% of the first content at the particular time.

30 After the pre-coalescing transient conversion is found to be within the most desired range, said pre-coalescing transient conversion continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range. As in previous embodiments, continuous monitoring and control are highly preferable, since the conditions in the reaction chamber may vary, causing changes in the pre-coalescing transient conversion values. Valves regulating ratios of liquids, and controlled by computerized controllers according to a desirable program are well known in the art.

In another embodiment of the present invention, better shown in Figure 4A, the reaction chamber 312 is provided a thermocouple 360a, positioned in the vicinity of the lower end 316, and shielded by shield 390. The thermocouple 360a is 5 electrically connected to the controller 335 through input line 360a' for providing pre-coalescing temperature data.

In operation of this embodiment, first reactant from line 370 and other liquids from line 371 are mixed in proportions regulated by the reactant mixing valve 369, in 10 order to produce the first liquid in line 342 so that said first liquid has a first content of first reactant.

A part of the droplets 348, produced and treated as described in the above embodiment, fall onto the thermocouple 360a, and their temperature is measured 15 by said thermocouple and provided to the controller 335 through input line 360a', where it is processed by well known to the art techniques. The controller 335 controls the reactant mixing valve through its output line 369'.

If the pre-coalescing temperature is above the predetermined pre-coalescing 20 temperature range, as earlier defined, the reactant mixing valve 369 is ordered by the controller 335 to lower the first content by decreasing the ratio of the first reactant from line 370 to liquids from line 371. Similarly, if the pre-coalescing temperature is under the predetermined pre-coalescing temperature range, according to this invention, the reactant mixing valve 369 is ordered by the 25 controller 335 to increase the first content by increasing the ratio of the first reactant from line 370 to liquids from line 371.

After the pre-coalescing temperature is found to be within the most desired range, said pre-coalescing temperature continues to be monitored with a goal in 30 most cases to stay somewhere in the vicinity of the middle value of said most desired range.

In still another embodiment of the present invention, better shown in Figure 5,

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the reaction chamber 412 is provided with an atomizer 426 in the vicinity of its upper end 414, and a sample collector 430 positioned in the vicinity of its lower end 416.

The atomizer 426 may be operable by gas or preferably without the need of gas

(usually referred to as "airless" in the art). The atomizer 426 of this embodiment is  
5 adapted to control at will the droplet size or diameter through a regulator 472. Such  
atomizers are well known in the art. For example, droplet diameter may change by  
changing the pressure of the liquid to be atomized, changing the orifice size,

changing the frequency and/or intensity in the case of ultrasonic or other pulsation  
operated atomizers, changing the pressure of the gas in the case of gas operated  
10 atomizers, changing the rotation or the speed in the case of centrifugal atomizers,  
etc. For the purposes of the instant invention, the regulator 472 represents any  
mechanism well known to the art, which is adapted to controllably change any  
variable parameter of the atomizer which controls average diameter of the droplets.

15 The sample collector 430 is connected to the conversion monitor or detector  
432 through sample line 433 for providing samples of droplets 448 trapped in the  
collector just (and coalesced, of course in the collector) before they coalesce onto  
the second liquid mass 454. The conversion monitor or detector 432 is connected,  
preferably electrically, to the controller 435 through input line 431 for transferring pre-  
20 coalescing transient conversion information. In turn, the controller 435 is connected,  
preferably electrically, to the regulator 472 through output line 472' in order to control  
said regulator 472. For purposes of clarity, basically only the elements of the device  
410, which illustrate this embodiment and its operation, are shown.

25 In operation of this embodiment, the first liquid containing the first reactant,  
cyclohexane for example, enters the reaction chamber 412 through line 442 in a  
manner that it is atomized by the atomizer 426, and forms a plurality of droplets 448.

30 A part of the droplets 448 fall into the sample collector 430, from where, they  
are directed to the conversion detector or monitor 432, to be analyzed regarding pre-  
coalescing transient conversion.

The information obtained in the conversion detector or monitor 432 is fed to computerized controller 435 through its input line 431, where it is processed by well known to the art techniques. The controller 435 controls the regulator 472 through its output line 472'.

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If the pre-coalescing transient conversion is above the pre-coalescing transient conversion range, as earlier defined, the regulator 472 is ordered by the controller 435 to increase the average diameter of the droplets. Similarly, if the pre-coalescing transient conversion is under the "pre-coalescing transient conversion range", according to this invention, the regulator 472 is ordered by the controller 435 to decrease the average diameter of the droplets.

The change in droplet diameter is preferably conducted in increments, preferably in the range of 10 to 20 % of the average droplet diameter at the particular 15 time.

After the pre-coalescing transient conversion is found to be within the most desired range, said pre-coalescing transient conversion continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of 20 said most desired range (about 40%, for example). As in previous embodiments, continuous monitoring and control are highly preferable, since the conditions in the reaction chamber may vary, causing changes in the pre-coalescing transient conversion values.

25 The device 410 may also optionally comprise an optical monitor 474, preferably of the fiber optic type, connected to an image analyzer 476 though line 474', which image analyzer is in turn connected to the computerized controller 435 through input line 476'. In operation of this arrangement, the image analyzer 476 determines the average droplet diameter from the image received from the optical 30 monitor 474, and sends this information to the controller 435, which then incorporates said information to the rest of the processed data, so that it can be better control the average droplet diameter, by comparing for example the change ordered to regulator 472 with the droplet size change as a result of it.

In another embodiment of the instant invention, better shown in Figure 5A, the thermocouple 460a is connected, preferably electrically, to the controller 435 through input line 460a' for transferring pre-coalescing temperature information. In 5 turn, the controller 435 is connected, preferably electrically, to the regulator 472 through output line 472' in order to control said regulator 472. For purposes of clarity, basically only the elements of the device 410, which illustrate this embodiment and its operation, are shown.

10 In operation of this embodiment, the first liquid containing the first reactant, cyclohexane for example, enters the reaction chamber 412 through line 442 in a manner that it is atomized by the atomizer 426, and forms a plurality of droplets 448.

15 A part of the droplets 448 fall onto the thermocouple 460a, and their temperature is measured and provided to computerized controller 435 through its input line 460a', where it is processed by well known to the art techniques. The controller 435 controls the regulator 472 through its output line 472'.

20 If the pre-coalescing temperature is above the predetermined pre-coalescing temperature range, as earlier defined, the regulator 472 is ordered by the controller 435 to increase the average diameter of the droplets. Similarly, if the pre-coalescing temperature is under the predetermined pre-coalescing temperature, according to this invention, the regulator 472 is ordered by the controller 435 to decrease the 25 average diameter of the droplets.

The change in droplet diameter is preferably conducted in increments, preferably in the range of 10 to 20 % of the average droplet diameter at the particular time.

30 After the pre-coalescing temperature is found to be within the most desired range (90 - 120° C, for example, in the case of cyclohexane to adipic acid, for example, under certain conditions), said pre-coalescing temperature continues to be

monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range (about 120° C, for example). As in previous embodiments, continuous monitoring and control are highly preferable, since the conditions in the reaction chamber may vary, causing changes in the pre-coalescing 5 temperature values. Valves regulating ratios of liquids, and controlled by computerized controllers according to a desirable program are well known in the art.

In a different embodiment of the present invention, better shown in Figure 6, the reaction chamber 512 is provided with an atomizer 526 in the vicinity of its upper 10 end 514, and a sample collector 530 positioned in the vicinity of its lower end 516. There is also provided a first liquid pump 577, which is adapted to regulate a first flow of the first liquid in line 542, and a flow meter 578 adapted to measure the rate of the first flow of the first liquid in line 542. The flow meter 578 is connected, preferably electrically, to the computerized controller 535 through input line 578'. The 15 sample collector 530 is connected to the conversion monitor or detector 532 through sample line 533 for providing samples of droplets 548 trapped in the collector just (and coalesced, of course in the collector) before they coalesce onto the second liquid mass 554. The conversion monitor or detector 532 is connected, preferably electrically, to the controller 535 through input line 531 for transferring pre-coalescing 20 transient conversion information. In turn, the controller 535 is connected, preferably electrically, to the first liquid pump 577 through output line 577' in order to control said first liquid pump 577. For purposes of clarity, basically only the elements of the device 510, which illustrate this embodiment and its operation, are shown.

25 In operation of this embodiment, the first liquid pump 577 pumps first liquid in line 542 at a desired first flow rate. Thus, the first liquid containing the first reactant, cyclohexane for example, in a first content, enters the reaction chamber 512 through line 542 in a manner that it is atomized by the atomizer 526 at a first flow rate, and forms a plurality of droplets 548.

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A part of the droplets 548 fall into the sample collector 530, from where, they are directed to the conversion detector or monitor 532, to be analyzed regarding pre-coalescing transient conversion.

The information obtained in the conversion detector or monitor 532 is fed to computerized controller 535 through its input line 531, where it is processed by well known to the art techniques. Also, the flow rate measurement from the flow meter

5 578 is fed to the controller 535 and processed in coordination with the information from line 531. The controller 535 in turn controls the first liquid pump 577 through its output line 577', in a manner to increase or decrease the flow rate of first liquid in a programmed manner.

10 If the pre-coalescing transient conversion is above the pre-coalescing transient conversion range, as earlier defined, the first liquid pump 577 is ordered by the controller 535 to increase the first flow rate, by increasing, for example, the pumping action. Similarly, if the pre-coalescing transient conversion is under the pre-coalescing transient conversion range, as earlier defined, the first liquid pump 577 is 15 ordered by the controller 535 to decrease the first flow rate, by decreasing, for example, the pumping action.

The change in first flow rate is preferably conducted in increments, preferably in the range of 5 to 10% of the first flow rate at the particular time.

20 25 After the pre-coalescing transient conversion is found to be within the most desired range, said pre-coalescing transient conversion continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range.

30 In a different embodiment of the present invention, better shown in Figure 6A, the reaction chamber 512 is provided with an atomizer 526 in the vicinity of its upper end 514, a thermocouple 560 positioned within the atomizer for monitoring the atomization temperature, and a thermocouple 560a, positioned in the vicinity of the lower end 516 of the reaction chamber 512. The thermocouples 560 and 560a are connected, preferably electrically, to the controller 535 through its input lines 560' and 560a', respectively, for providing atomization temperature and pre-coalescing temperature data to said controller 535. In turn, the controller 535 is

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connected, preferably electrically, to the first liquid pump 577 through output line 577' in order to control said first liquid pump 577. For purposes of clarity, basically only the elements of the device 510, which illustrate this embodiment and its operation, are shown.

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In operation of this embodiment, the first liquid pump 577 pumps first liquid in line 542 at a desired first flow rate. Thus, the first liquid containing the first reactant, cyclohexane for example, in a first content, enters the reaction chamber 512 through line 542 in a manner that it is atomized by the atomizer 526 at a first flow rate, and forms a plurality of droplets 548.

10 A part of the droplets 548 fall onto thermocouple 560a, where their temperature is measured and fed to computerized controller 535 through its input line 560a', where it is processed by well known to the art techniques. Also, the 15 atomization temperature, measured by thermocouple 560 is fed to the controller 535 through its input line 560', where it is also processed. The flow rate measurement from the flow meter 578 is fed to the controller 535 through input line 578' and processed in coordination with the information from input lines 560a' and 560'. The controller 535 in turn controls the first liquid pump 577 through its output line 577', in 20 a manner to increase or decrease the flow rate of first liquid in a programmed manner.

25 If the prevailing determinant (pre-coalescing temperature or transient temperature difference in this case) is above the prevailing determinant desired range, as defined earlier, the first liquid pump 577 is ordered by the controller 535 to increase the first flow rate, by increasing, for example, the pumping action. Similarly, if the prevailing determinant is under the prevailing determinant desired range, as earlier defined, the first liquid pump 577 is ordered by the controller 535 to decrease the first flow rate, by decreasing, for example, the pumping action.

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The change in first flow rate is preferably conducted in increments, preferably in the range of 5 to 10% of the first flow rate at the particular time.

After the prevailing determinant is found to be within the most desired range, the prevailing at the time determinant continues to be monitored with a goal in most cases for both determinants to stay somewhere in the vicinity of the middle value of their most desired range, as already explained.

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In still a different embodiment of the present invention, better shown in Figure 7, the reaction chamber 612 is provided with an atomizer 626 in the vicinity of its upper end 614, and a sample collector 630 positioned in the vicinity of its lower end 616. There is also provided a volatiles mixing valve 679, which is adapted to mix 10 volatiles from line 680 and other liquids from line 681 in order to produce the first liquid in line 642. The sample collector 630 is connected to the conversion monitor or detector 632 through sample line 633 for providing samples of droplets 648 trapped in the collector just (and coalesced, of course in the collector) before they coalesce 15 onto the second liquid mass 654. The conversion monitor or detector 632 is connected, preferably electrically, to the controller 635 through input line 631 for transferring pre-coalescing transient conversion information. In turn, the controller 635 is connected, preferably electrically, to the volatiles mixing valve 679 through output line 679' in order to control said volatiles mixing valve 679. For purposes of clarity, basically only the elements of the device 610, which illustrate this 20 embodiment and its operation, are shown.

In operation of this embodiment, volatiles from line 680 and other liquids from line 681 are mixed in proportions regulated by the volatiles mixing valve 679, in order to produce the first liquid in line 642 so that said first liquid has a desired content of 25 volatiles. The volatiles are substances, of usually lower boiling point than that of the first reactant, which under the conditions of the reaction have a tendency to volatilize as the first liquid is atomized in the reaction chamber and lower conversion rates. The volatiles have preferably low or no reactivity under the reaction conditions. In 30 the case of oxidation of cyclohexane to adipic acid, acetic acid and/or acetone, for example, would represent volatiles.

The liquids from line 681 contain first reactant, along with solvents, catalysts, promoters, initiators, recycled ingredients, and the like. The first liquid containing the

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first reactant, cyclohexane for example, enters the reaction chamber 612 through line 642 in a manner that it is atomized by the atomizer 626, and forms a plurality of droplets 648.

5 A part of the droplets 648 fall into the sample collector 630, from where, they are directed to the conversion detector or monitor 632, to be analyzed regarding pre-coalescing transient conversion.

10 The information obtained in the conversion detector or monitor 632 is fed to computerized controller 635 through its input line 631, where it is processed by well known to the art techniques. The controller 635 controls the volatiles mixing valve 679 through its output line 679'.

15 If the pre-coalescing transient conversion is above the pre-coalescing transient conversion range, as earlier defined, the volatiles mixing valve 679 is ordered by the controller 635 to increase the introduction of volatiles from obtained from line 680. Similarly, if the pre-coalescing transient conversion is under the "pre-coalescing transient conversion range", according to this invention, the volatiles mixing valve 679 is ordered by the controller 635 to decrease or eliminate the introduction of volatiles from line 680.

20 The increase or decrease of volatiles is preferably conducted in increments, preferably in the range of 2 to 5% based on the total weight of the first liquid at that particular time.

25 After the pre-coalescing transient conversion is found to be within the most desired range, said pre-coalescing transient conversion continues to be monitored with a goal in most cases to stay somewhere in the vicinity of the middle value of said most desired range.

30 If the liquids in line 681 are arranged to contain no or only small amounts of catalyst, then catalyst may be added through line 680 at a desired base level. Addition of higher amounts of catalyst will favor increase of pre-coalescing transient

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conversion, while addition of lower amounts of catalyst will favor decrease of pre-coalescing transient conversion.

5 The increase or decrease of catalyst level is preferably conducted in increments, preferably in the range of 5 to 10% based on the total weight of the catalyst contained in the first liquid at that particular time.

In still a different embodiment of the present invention, better shown in Figure 7A, the reaction chamber 612 is provided with an atomizer 626 in the vicinity 10 of its upper end 614, a thermocouple 660 within the atomizer 626, and a thermocouple 660a positioned in the vicinity of its lower end 616. The thermocouple 660a is connected, preferably electrically, to the controller 635 through input line 660a' for providing pre-coalescing temperature information to said controller 635.

15 In operation of this embodiment, volatiles from line 680 and other liquids from line 681 are mixed in proportions regulated by the volatiles mixing valve 679, in order to produce the first liquid in line 642 so that said first liquid has a desired content of volatiles.

20 The liquids from line 681 contain first reactant, along with solvents, catalysts, promoters, initiators, recycled ingredients, and the like. The first liquid containing the first reactant, cyclohexane for example, enters the reaction chamber 612 through line 642 in a manner that it is atomized by the atomizer 626, and forms a plurality of droplets 648.

25 The atomization and pre-coalescing temperature information obtained by thermocouples 660a and 660 is fed to computerized controller 635 through its input lines 660a' and 660, respectively, where it is processed by well known to the art techniques according to a desired program. The controller 635 controls the volatiles 30 mixing valve 679 through its output line 679'.

A part of the droplets 648 fall into the sample collector 630, from where, they are directed to the conversion detector or monitor 632, to be analyzed regarding

prevailing determinant.

If the prevailing determinant is above the prevailing determinant predetermined range, as earlier defined, the volatiles mixing valve 679 is ordered by the controller 635 to increase the introduction of volatiles from obtained from line 680. Similarly, if the prevailing determinant is under the prevailing determinant predetermined range, according to this invention, the volatiles mixing valve 679 is ordered by the controller 635 to decrease or eliminate the introduction of volatiles from line 680.

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After the prevailing determinant is found to be within the most desired range, the prevailing at the time determinant continues to be monitored with a goal in most cases for both determinants to stay somewhere in the vicinity of the middle value of their most desired range, as already explained.

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Again, if the liquids in line 681 are arranged to contain no or only small amounts of catalyst, then catalyst may be added through line 680 at a desired base level. Addition of higher amounts of catalyst will favor increase of pre-coalescing temperature, transient temperature difference and pre-coalescing transient conversion, while addition of lower amounts of catalyst will favor decrease of pre-coalescing temperature, transient temperature difference, and pre-coalescing transient conversion.

In still another embodiment, better shown in Figure 8, the reaction chamber 25 712 is provided with an atomizer 726 in the vicinity of its upper end 714, and a sample collector 730 adapted to be floating as a boat on liquid 754 at the lower end 716 of the reaction chamber 712. The sample collector 730, also supports a thermocouple 760a for measuring pre-coalescing temperature. The atomizer 726 is provided with first liquid from line 742, which contains a flow meter 778. There is 30 also provided a retaining tank 753, connected to the vicinity of the lower end 716 of the reaction chamber 712 through two pumps 751a and 751b. The retaining tank 753 is also connected to pump 751c, which is adapted to transfer liquid to a separator (shown as 15 in Figure 1). There is further provided a level controller 755,

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which controls pump 751c, based on the level of liquid in retaining tank 753, by well known to the art techniques. The level controller activates pump 751c through output line 751c' when the liquid exceeds level A, and deactivates said pump 751c when the liquid goes lower than level B.

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The sample collector 730 is connected to the conversion monitor or detector 732 through sample line 733, which has a flexible coiled portion 733' for providing samples of droplets 748 trapped in the collector just (and coalesced, of course in the collector) before they coalesce onto the second liquid mass 754. The sample 10 collector 730 has a boat like configuration provided with a closed float portion 730a, and a sample portion 730b, as better shown in Figure 9. The flexible coiled portion 733' of line 733, and the flexible coiled portion 760a" of the line 760a' allow the boat-like sample collector 730 to move freely along with the surface 756 of the second 15 liquid mass 754. The thermocouple 760a, supported by the floating sample collector 730, is connected to the controller 735 through input line 760a', which has the coiled portion 760a". The thermocouple transfers, preferably electrically, pre-coalescing temperature data to the controller 735.

The conversion monitor or detector 732 is also connected, preferably 20 electrically, to the controller 735 through input line 731 for transferring pre-coalescing transient conversion information. Also the flow meter 778 is connected, preferably electrically, to the controller 735 through input line 778' for transferring flow rate information regarding the first liquid entering the reaction chamber 712 through the atomizer 726. In turn, the controller 735 is connected, preferably 25 electrically, to pumps 751a and 751b through output lines 751a' and 751b, respectively, for controlling said pumps 751a and 751b.

For purposes of clarity, basically only the elements of the device 710, which illustrate this embodiment and its operation, are shown.

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In operation of this embodiment, the first liquid containing the first reactant, cyclohexane for example, enters the reaction chamber 712 through line 742 in a manner that it is atomized by the atomizer 726, and forms a plurality of droplets

748.

A part of the droplets 748 fall into the sample collector 730, from where, they are directed through line 733 and its flexible portion 733' to the conversion detector or monitor 732, to be analyzed regarding pre-coalescing transient conversion. Part of the droplets also fall onto the thermocouple 760a, which measures the pre-coalescing temperature, and then transfers this information to the controller 735 through line 760a' and through its coiled portion 760a".

10 The information obtained in the conversion detector or monitor 732 is also fed to the computerized controller 735 through its input line 731, where it is processed by well known to the art techniques. The controller 735 controls pumps 751a and 751b, as aforementioned.

15 If the prevailing determinant (pre-coalescing temperature or pre-coalescing transient conversion), as earlier explained, is above the predetermined prevailing determinant range, as earlier defined, pump 751a is ordered by the controller 735 to stop its pumping action, and pump 751b is activated. This causes the surface 756 of the second liquid mass 754 to rise, resulting in smaller atomization distance, as 20 defined earlier. In turn, smaller atomization distance causes the prevailing determinant to decrease. Similarly, if the prevailing determinant is under the predetermined prevailing determinant range, as earlier defined, pump 751a is ordered by the controller 735 to start or continue its pumping action, and pump 751b is deactivated. This causes the surface 756 of the second liquid mass 754 to drop, 25 resulting in higher atomization distance. In turn, higher atomization distance causes the prevailing determinant to increase.

The level 756 of the second liquid mass 754 may be determined by the controller 735 either indirectly by correlating the amounts of incoming first liquid 30 (through the atomizer, as measured by the flow meter 778 and obtained by the controller 735 through line 778', and through pump 751b) and outcoming second liquid 754 through pump 751a, or directly by use of a level measuring device (not shown for purposes of clarity) in the reaction chamber. Level measuring devices are

well known in the art.

The level of liquids in the retaining tank 753 is controlled by level controller 755. When the level goes under level B, pump 751c is deactivated by the controller 5 755. If the liquid level exceeds level A, pump 751c is activated again by controller 755. The retaining tank 753 should contain enough liquid at its lowest level B to take care of any given variations of liquid level 756 in the reaction chamber 712.

The increase or decrease of atomization distance is preferably conducted in 10 increments, preferably in the range of 2 to 5% of the atomization distance at the time the measurement is made.

After the prevailing determinant is found to be within the most desired range, the prevailing at the time determinant continues to be monitored with a goal in most 15 cases for both determinants to stay somewhere in the vicinity of the middle value of their most desired range, as already explained. As in previous embodiments, continuous monitoring and control of all determinants are highly preferable, since the conditions in the reaction chamber may vary, causing changes in the determinant values. Valves regulating ratios of liquids, and controlled by computerized controllers 20 according to a desirable program are well known in the art.

Going back to Figure 1, the separator 15, as aforementioned, can be any assembly of equipment, simple or complicated, which is capable of separating the intermediate oxidation product from the second liquid. Such equipment is well known 25 to the art, as described for example in a plethora of patents regarding separation of adipic acid from the mother liquor (second liquid in this case).

In the case that the oxidation product is a solid having limited solubility in the second liquid, either at the reaction temperature or any other temperature, as is the 30 case of adipic acid in the case of its production from oxidation of cyclohexane, the separator 15 may comprise, according to this invention, two filters 15a and 15b connected in parallel, as better shown in Figure 10. The separator 15 may also comprise valves 15w, 15x, 15y, and 15z, as well as an optional heat removal device

15i, which may take the form of a crystallizer.

In operation of this separator, valves 15x and 15y are initially open, while valves 15w and 15z are closed. While valves 15w and 15z are closed, any solid oxidation product previously accumulated in filter 15a, such as adipic acid for example, is separated from said filter 15a, either manually or automatically (back-flush, scraping, and the like well known to the art, for example / not shown). Second liquid from line 24, optionally passing through heat removal device 15i for changing the liquid temperature to a more appropriate temperature for the solid separation, passes through filter 15b, where the solid oxidation product is removed from the second liquid, which second liquid follows line 11 for recirculation to the recirculation tank 19 (Figure 1) or further processing in other equipment (not shown). When filter 15a has been substantially emptied, and filter 15b has been substantially full or otherwise ready for being emptied, valves 15w and 15z are opened and valves 15x and 15y are closed, so that filtering of solid oxidation product takes place now in filter 15a, while filter 15b is being emptied. This cycle is repeated in the process. Of course, alternate devices may be used, such as for example, rotary drum filters and the like.

20 In a different embodiment of this invention, better shown in Figure 11, the apparatus or device 810 of the present invention, also comprises a condenser 857 connected to the gas outlet 823 through line 825, and to condensate tank 859, which serves as a reservoir of condensate collected from condenser 857. The condensate tank 859, through valve 865 is connected to line 865', which in turn is connected to the liquid dispensing ring 844, or it is connected to line 865", which in turn leads to line 811 for recycling the condensed liquids to the recycling tank 819. The valve 865 is adapted to direct the condensed liquids totally to line 865', or totally to line 865", or partially to line 865' and partially to line 865", or be closed and not permit any transfer of condensed liquids.

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The device 810 also comprises a heat exchanger 838 connected to the recycling tank 819; an eductor or aspirator 861, connected to the heat exchanger 838; a pump 877 connected to the eductor 861 at the intake and to the atomizer 826

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at the other end. The eductor 861 is adapted to produce vacuum to line 867' through regulating valve 867 (when the regulating valve 867 is in an open position) and through check valve 867a, which allows flow from line 867' toward the pump but not vice versa. Line 867' is connected to line 857' between the condenser 857 and the 5 valve 864. An additional pump (not shown) may be placed between the eductor 861 and the heat exchanger 838, which in coordination with pump 877 may control the vacuum produced by the eductor 861 toward line 867'. It may be also utilized to prevent starvation of pump 877 from first liquid. The heat exchanger 838 may be part 10 of the condenser 857 (not shown as such in Figure 11), so that heat received from condensables is used as heat source for the heat exchanger 838.

Lines 841a, 841b, and 841c are used to supply the recirculation tank with appropriate amounts of raw materials, catalysts, solvents, initiators, promoters and the like.

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In operation of this embodiment, first liquid from the recycling tank is heated to the desired temperature in heat exchanger 838. The heated first liquid is pumped through pump 877 to the atomizer 826, where it is broken into droplets 848, which finally coalesce onto the second liquid 854 as already discussed in previous 20 embodiments. At the same time, gas containing an oxidant, preferably oxygen, enters the reaction chamber 812 in a counterflow direction with regard to the droplets, as also discussed earlier, and the oxidant reacts with the first reactant contained in the droplets of the first liquid. Any off-gases produced during the reaction, which are usually non-condensable unless subjected to extremely low 25 temperatures, along with condensables leave the reaction chamber 812 through gas outlet 823. Following line 825, they enter the condenser 857, where the condensables condense to condensate, which condensate is accumulated into the condensate tank 859.

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If it is desired to form a curtain or thick film 845, the condensate is directed, at least partially, through valve 865 to line 865', from where it is fed to the liquid dispensing ring 844 and forms said curtain 845, useful to prevent sticking of any reaction or other solid products to the walls of the reactor 812. This condensate has

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the advantage over the recycled liquid coming through line 11' of Figure 1, for example, that in most cases it is substantially catalyst free. This is because in the practice of this invention, non volatile catalysts, such as metal salts for example, are utilized in most occasions.

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If no condensate is needed to supply the liquid dispensing ring, the 865 is caused to direct the condensate to line 865", which feeds it to line 811, so that the condensate is finally transferred to the recirculation tank 819. In general, as aforementioned, the valve 865 is adapted to direct the condensed liquids totally to 10 line 865', or totally to line 865", or partially to line 865' and partially to line 865", or be closed and not permit any transfer of condensed liquids.

The non-condensable gases follow line 857', and exit the system through valve 864, if so desired. Valve 864, as also shown in other embodiments, is 15 preferably controllable to open and close to any degree demanded by the operation. If it is desired to remove all non-condensable gases from the system, valve 864 is opened to a desired degree for the pressure inside the system to be maintained to desired levels, and valve 867 is completely closed. If it is desired to only partially remove non-condensables, both valves 864 and 867 are opened to the desired 20 degree, so that vacuum formed by the eductor or aspirator 861, recirculates the part of non-condensables caused by the vacuum to enter the reaction chamber 812. Complete recirculation of non-condensables without any non-condensables leaving the system is only possible if no new flow of gas containing oxidant takes place after a certain point, so that the pressure inside the reaction chamber 812 will not finally 25 exceed predetermined limits. Check valve 867a does not hinder the flow of non-condensables, but it prevents entry of first liquid to line 867' in case of accidental flooding of the aspirator 861.

In still a different embodiment of this invention, better shown in Figure 12, the 30 apparatus or device 910 of the present invention, also comprises a condenser 957 connected to the gas outlet 923 through line 925, and to condensate tank 959, which serves as a reservoir of condensate collected from condenser 957. The condensate tank 959, is connected to the liquid dispensing ring 944. The condenser 957 is also

connected to a valve 964 through line 957', which valve is adapted to release non-condensables, if in an open position.

The device 910 also comprises a heat exchanger 938 connected to the  
5 recycling tank 919 and to the atomizer 926 at the other end. It also comprises a gas pump 961 connected to line 957' through line 967' adapted to transfer non-condensables from line 957' to the gas inlet feed line 936. A replenish gas line 936' is also connected to line 936 for providing fresh gas containing oxidant, preferably oxygen.

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The heat exchanger 938 may be part of the condenser 957 (not shown as such in Figure 11), so that heat received from condensables is used as heat source for the heat exchanger 938.

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Lines 941a, 941b, and 941c are used to supply the recirculation tank with appropriate amounts of raw materials, catalysts, solvents, initiators, promoters and the like.

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In operation of this embodiment, first liquid from the recycling tank is heated to the desired temperature in heat exchanger 938, and enters the atomizer 926, where it is broken into droplets 948, which finally coalesce onto the second liquid 954 as already discussed in previous embodiments. At the same time, gas containing oxidant, preferably oxygen, enters the reaction chamber 912 through line 936 in a counterflow direction with regard to the droplets, as also discussed earlier, and the 25 oxidant reacts with the first reactant contained in the droplets of the first liquid. Any off-gases produced during the reaction, which are usually non-condensable unless subjected to extremely low temperatures, along with condensables leave the reaction chamber 912 through gas outlet 923. Following line 925, they enter the condenser 957, where the condensables condense to a condensate, which condensate is 30 accumulated into the condensate tank 959.

The condensate is directed, at least partially as discussed in other embodiments, to the liquid dispensing ring 944 and forms curtain 945, useful to

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prevent sticking of any reaction or other solid products to the walls of the reactor 912. This condensate has the advantage over the recycled liquid coming through line 11' of Figure 1, for example, that in most cases it is substantially catalyst free. This is because in the practice of this invention, non volatile catalysts, such as metal salts 5 for example, are utilized in most occasions.

If no condensate is needed to supply the liquid dispensing ring 944, the condensate may be directed elsewhere through line 959'.

10 The non-condensable gases follow line 957', and exit the system through valve 964, if so desired. Valve 964, as also shown in other embodiments, is preferably controllable to open and close to any degree demanded by the operation. If it is desired to remove all non-condensable gases from the system, valve 964 is 15 opened to a desired degree for the pressure inside the system to be maintained to desired levels, and pump 961 is deactivated. If it is desired to have only partial removal of non-condensables, valve 964 is opened to the desired degree, and pump 961 is also activated to the desired degree so that this combination causes recirculation of part of non-condensables to the reaction chamber 912. Complete 20 recirculation of non-condensables without substantially any non-condensables leaving the system may be preferably conducted by not allowing new flow of inert gas diluents to take place after a certain point, so that the pressure inside the reaction chamber 912 does not finally exceed predetermined limits.

25 The second liquid 954 is directed to the separator 915, through line 924, where the intermediate oxidation product is separated and the remaining liquids are either sent to another separator (not shown) for further separation of constituents, or they are directed to the recycling tank 919 for recycling, or a combination thereof.

30 In another embodiment of this invention, better shown in Figure 13, the reaction chamber 1012 has a gas outlet 1023, which coincides with the liquid outlet 1022, preferably in the vicinity of the lower end 1016 of the reaction chamber 1012. Both the gas distributor 1073 fed by gas inlet line 1036, and the atomizer 1026 fed by line 1042, are preferably disposed at the upper end 1014 of the reaction chamber

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1012. The gas distributor 1073 and the atomizer 1026 may be combined into one unit, and the gas may be used to help or totally be responsible for the atomization process.

5        The liquid/gas output 1022/1023 has preferably a conical shape of reduced diameter as compared to the diameter of the reaction chamber 1012, as illustrated in Figure 13. The liquid dispensing ring 1044 is preferably positioned either at the bottom of the reaction chamber as shown in Figure 13, or at the top 1023' of the liquid/gas output 1022/1023. Preferably, the liquid dispensing ring 1044 is adapted 10 to deliver the liquids in a swirling manner. A cooler (not shown) may be placed in line 1011' in order to cool the liquids to a desired temperature adequate to condense condensables exiting from the reaction chamber 1012 through the liquid/gas output 1022/1023.

15        There is also provided a liquid/gas separator 1075 for receiving the condensed condensables and the non-condensables from the reaction chamber 1012 through line 1025 and separating the second liquid 1054 from the non-condensables. The liquid/gas separator 1075 is in turn connected to separator 1015, which is adapted to separate the intermediate oxidation product from the reactants and other 20 materials introduced into the system in the process.

In operation of this embodiment, first liquid is introduced to the atomizer 1026 through line 1042, where it is broken into droplets 1048, which finally coalesces in the vicinity of the lower end 1016, preferably on the curtain or thick film 1045 and 25 within the liquid/gas output 1022/1023. At the same time, gas containing an oxidant, preferably oxygen, enters the reaction chamber 1012 in the same direction with regard to movement of the droplets, and the oxidant reacts with the first reactant contained in the droplets of the first liquid as both droplets and gas travel in a direction from the upper end 1014 to the lower end 1016 of the reaction chamber 30 1012. Condensables condense on the swirling cold liquids entering the system through line 1011'. The liquids coming in the reaction chamber through line 1011' may be derived from within the system or from outside the system. Any off-gases produced during the reaction, which are usually non-condensable unless subjected to

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low temperatures, along with condensibles leave the reaction chamber 1012 through the liquid/gas output 1022/1023. Following line 1025, they enter the liquid/gas separator 1075, where the second liquid 1054 is separated from the non-condensibles, which are removed through line 1057' and valve 1064, which valve 5 may operate as already discussed in previous embodiments.

The second liquid 1054 is directed to the separator 1015, where it is treated as already discussed in previous embodiments.

10 As mentioned earlier, condensation of condensibles may be inside the pressurized device, such as for example device 810 and 910 of Figures 11 and 12, respectively, in the respective condensers 857 and 957, before the respective valves 864 and 964, which are used to purge the non condensibles, such as miscellaneous off-gases, which may include one or more of oxygen, nitrogen, carbon 15 monoxide, carbon dioxide, and the like, for example. This particular type of condensation, albeit outside the reaction chamber, is by definition internal condensation, according to this invention, and it takes place at a pressure which is substantially the same as the reaction pressure.

20 According to this invention, internal condensation inside the reactor may also take place, and in most occasions it is preferable to the outside internal condensation. Internal condensation (before substantial pressure drop) is highly preferable to external condensation (after substantial or total pressure drop). Internal inside condensation is especially suitable in the case of employing close to 25 stoichiometric amounts of oxidant for the oxidation process.

One embodiment of the instant invention utilizing internal inside condensation is better shown in Figure 14, wherein only a limited number of elements is shown, for purposes of clarity. There is provided a cooling mantle 1183 surrounding the reaction 30 chamber 1112 in all or part of its height. Otherwise, the reaction chamber 1112 comprises the same elements as in the previous embodiments.

The operation of this embodiment is similar to the operation of the previous

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embodiments with the exception that a cooler enters the mantle 1183 through line 1182 and exits through line 1182'. The temperature of the cooler is such as to cool down the wall 1120 adequately for vapors of condensibles inside the reaction chamber to condense and form a thick film or curtain 1145. Since the catalyst (metal salt for example, such as cobalt acetate, for example) in most cases is not volatile, it does not transfer to this curtain. Further, the temperature of the thick film is lower than that of the temperature of the droplets. Thus, no substantial reaction takes place within the curtain, and in addition to other advantages, the thick film or curtain 1145 prevents solid buildup on the walls of the condenser.

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Another embodiment of the instant invention utilizing internal inside condensation is better shown in Figure 15, wherein only a limited number of elements is shown, for purposes of clarity. There is provided a cooling coil 1283 inside the reaction chamber 1212, having an entry coolant line 1282 and a coolant exit line 1282'. The coil may be extending through the whole height of the reactor or just through part of it. The coil 1283 may be positioned vertical as shown in Figure 15, or horizontal, or it may have any other suitable for the circumstances direction. Otherwise, the reaction chamber 1212 comprises the same elements as in the previous embodiments.

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The operation of this embodiment is similar to the operation of the previous embodiments with the exception that a cooler enters the coil 1283 through line 1282 and exits through line 1282'. The temperature of the cooler is such as to cool down the coil 1283 adequately for vapors of condensibles inside the reaction chamber to condense on said coil 1283. Since the catalyst (metal salt for example, such as cobalt acetate, for example) in most cases is not volatile, it does not transfer to the condensate on the coil. Further, the temperature of the condensate on the coil 1283 is lower than that of the temperature of the droplets. Thus, reactants and catalysts contained in droplets coalescing on the coil are considerably diluted, and no substantial reaction takes place within a thick film (not shown) formed on the coil from condensate and coalesced droplets. The thick film also prevents solid buildup on the coil.

Still another embodiment of the instant invention utilizing internal inside condensation is better shown in Figure 16, wherein only a limited number of elements is shown, for purposes of clarity. There is provided a cooling liquid sprayer 1385, preferably at the upper end 1314 of the reaction chamber 1312, and even more preferably disposed on top of the atomizer 1326, having an entry cooling liquid line 1384. Otherwise, the reaction chamber 1312 comprises the same elements as in the previous embodiments.

The operation of this embodiment is similar to the operation of the previous embodiments with the exception that a cooling liquid enters the cooling liquid sprayer 1385 through line 1384. It is then atomized by sprayer 1385. The cooling liquid comprises preferably either the same solvent contained in the first liquid or first reactant contained in the first liquid. For example, in the case of preparation of adipic acid from cyclohexane, the cooling liquid preferably comprises acetic acid (solvent), or cyclohexane (first reactant), or a mixture thereof. Preferably, no catalyst is contained in the cooling liquid. The temperature at which the cooling liquid is atomized is such that condensables condense on the droplets of the atomized cooling liquid, thus providing internal inside condensation. As aforementioned, the droplets of the first liquid do not mix with the cooling liquid droplets, for all practical purposes, while both are being suspended in the gas, so that oxidation proceeds unhindered within the droplets of the first liquid. Finally, both types of droplets coalesce together at the lower end 1316 of the reaction chamber 1312 to form the second liquid 1353, which is removed through line 1324 for further treatment, as described in previous embodiments. In determination of the pre-coalescing transient conversion, the flow rate of the cooling liquid and the flow rate of the first liquid have to be taken into account by well known to the art techniques in the controller (for example shown as 35 in Figure 1).

A different embodiment of the instant invention utilizing internal inside condensation is better shown in Figure 17, wherein only a limited number of elements is shown, for purposes of clarity. There is provided a cooling liquid sprayer 1485, preferably at the upper end 1414 of the reaction chamber 1412 having an entry cooling liquid line 1484. The sprayer 1485 has preferably a plurality of spray

nozzles 1486 around its perimeter. The spray nozzles 1486 are directed toward the wall 1420 of the reaction chamber 1412. Otherwise, the reaction chamber 1412 comprises the same elements as in the previous embodiments.

5 The operation of this embodiment is similar to the operation of the previous embodiments with the exception that a cooling liquid enters the cooling liquid sprayer 1485 through line 1484. It is then atomized by sprayer 1485 through nozzles 1486, and falls on the walls 1420 of the reaction chamber 1412, where it forms a thick film or curtain 1445. The cooling liquid comprises preferably either the same solvent  
10 contained in the first liquid or first reactant contained in the first liquid. For example, in the case of preparation of adipic acid from cyclohexane, the cooling liquid preferably comprises acetic acid (solvent), or cyclohexane (first reactant), or a mixture thereof. Preferably, no catalyst is contained in the cooling liquid. The temperature at which the cooling liquid is atomized is such that condensibles  
15 condense on the droplets of the atomized cooling liquid, and also on the curtain 1445, thus providing internal inside condensation. Since the catalyst (metal salt for example, such as cobalt acetate, for example) in most cases is not volatile, it does not transfer to the curtain 1445. Further, the temperature of the thick film is lower than that of the temperature of the first liquid droplets. Thus, no substantial reaction  
20 takes place within the curtain 1445, and in addition to other advantages, the thick film or curtain 1445 prevents solid buildup on the walls of the condenser. Liquids and droplets are finally mixed together at the lower end 1416 of the reaction chamber 1412, as the second liquid 1454, which is removed through line 1424 for further treatment, as described in previous embodiments.

25 In another embodiment of the present invention, better shown in Figure 18, there is provided one or more thermocouples 1560b and/or sample collectors 1530', arranged within the reaction zone 1534, which are connected to a preferably computerized controller (not shown). The thermocouples 1560b and/or sample  
30 collectors 1530' may be positioned in any appropriate places of the reaction zone 1534 in order to monitor the temperature and/or conversion of the falling droplets at different distances between the upper end 1532 and the lower end 1542 of the reaction chamber 1522.

In operation of this embodiment the thermocouples 1560b take the temperature of the droplets and feed this information to the controller (not shown), as described in previous embodiments. Similarly, the sample collectors provide 5 coalesced liquid from the falling droplets to a conversion monitor (not shown), which in turn provides conversion information to the controller (not shown), as described in previous embodiments. The controller, based on this information, gives appropriate orders to the other components of the device to prevent the temperature from deviating outside predetermined limits, if so desired, not only for purposes of 10 controlling the reaction but also to prevent catastrophic results in case that the reaction heat released is excessive. This presents an additional safeguard.

Although one thermocouple, preferably close to the lower end 1542, may be used for monitoring temperature, it is more preferable to use more than one 15 thermocouples 1560b in the reaction zone 1534 for determining the rate of temperature rise, or temperature profile in the droplet path. The temperature difference between two of these thermocouples is called transient temperature sub-difference. The higher the temperature changes from thermocouple to thermocouple (transient temperature sub-difference) the more drastic the changes ordered by the 20 controller.

In a different preferred embodiment of the present invention, better shown in Figure 19, there is depicted a device 1610 for preparing an intermediate oxidation product from a first liquid containing a first reactant and a gas containing a second 25 reactant. The device 1610 comprises a reaction chamber 1612, which chamber has an upper end 1614, and a lower end 1616. The chamber 1612 is preferably of cylindrical shape turning to conical at the vicinity of the lower end 1616, and finally leading to a liquid outlet 1622 connected to an outlet line 1624. The outlet line 1624 leads to a pump 1618, which is connected to a first valve 1619 through line 30 1624a. The first valve 1619 is adapted to connect line 1624a to either line 1624b or line 1624c or partially to line 1624b and partially to line 1624c. Line 1624b leads back to the reaction chamber 1612 (through line 1642) at an atomizer 1626, preferably located at the upper end 1614 of the reaction chamber 1612. The

atomizer 1626 has preferably a plurality of nozzles 1627, which more preferably are of the airless type, well known in the art. The atomizer 1626 may be steady at a certain position of the reaction chamber 1612, or it may be movable, preferably in an up/down mode, as previously described, for example.

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Line 1624c leads to a second valve 1619a, which is adapted to connect line 1624c to either line 1624d, or line 1624f, or partially to line 1624d and partially to line 1624f. Line 1624d leads to a separator 1615 where the intermediate oxidation products are separated from reactants, unreacted reactants, usually containing 10 various amounts of intermediate oxidation products, solvents, catalysts, and other adjuncts, return to a recirculation tank (not shown) through line 1611. The separator may be as simple a device as a filter, or as complicated as a battery of tanks, washers, extractors, distillation columns, etc., suitable to each particular case, as also described previously. Line 1624f leads to a device 1612a, which may 15 be another reaction chamber or a battery of reaction chambers, or other devices including but not limited to tanks, washers, extractors, distillation columns, etc. The device 1612a is connected to separator 1615 through line 1611a, especially in the case that device 1612a is a simple reaction chamber or a battery of reaction chambers.

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At the vicinity of the upper end 1614 of the reaction chamber 1612, there is provided a gas outlet 1623 leading to an outlet gas line 1625.

A gas inlet 1634, preferably located in the vicinity of the lower end 1616 of 25 the reaction chamber 1612, is connected to a gas inlet feed line 1636, which provides the gas containing the second reactant, which is preferably an oxidant, such as oxygen for example.

A thermocouple 60, or other temperature measuring means, is preferably 30 disposed within the atomizer in order to measure the atomization temperature, which is the temperature of the first liquid just before being atomized. One or more thermocouples 60a are disposed within the reaction chamber 1612, while thermocouple 60b is disposed within the second liquid 1654 at the lower part of the

reaction chamber 1612, in order to measure the temperature of the second liquid 1654.

Within the reaction chamber 1612, there is also provided a (one or more) 5 sample collector 1630, which is adapted to collect droplets of liquid and transfer them preferably as a miniature stream of liquid to a conversion detector (the word detector according to the present invention includes the meaning of monitor) 1632 through sample line 1633, as also previously described. The conversion detector 1632 may also monitor the amount of first reactant and the amount of the 10 intermediate oxidation product as the first liquid enters the atomizer through appropriate sample line(s), not shown for purposes of clarity. This information along with information on the nature and quantity of what is added in line 1641, for example, can accurately determine the amounts of intermediate oxidation product and first reactant going to the atomizer 1626. The conversion in the second liquid 15 1654 may also be detected and monitored through sample line 1633', which connects line 1624a with the conversion detector 1632.

The device 1610 also comprises a controller 1635, preferably computerized, which is fed information regarding temperature through input lines 60', 60a' and 20 60b'. The controller 1635 is also fed information regarding conversion of reactants to intermediate oxidation product from detector 1632 through input line 1631. In turn, the controller 1635 controls, through one or more output lines 1636, any of a plurality of means for adjusting conversions and/or temperatures in order to control the oxidation rate, as described in detail earlier. Such means and their operation, 25 examples of which have been described earlier, include but are not limited to heat exchangers (for example heat exchanger 1645 in line 1642), and other means for changing the atomization temperature, the reaction pressure, the atomization distance, the average droplet diameter, the first flow rate (rate of production of droplets from the first liquid), the second flow rate (flow rate of the gas), the 30 volatilization rate (volatilization of volatile ingredients contained in the droplets), the first content (the content of first reactant in the first liquid), the second content (content of second reactant, preferably oxidant in the gas), the catalyst content (in the first liquid), and a combination thereof. For purposes of brevity and clarity these

means have not been include in Figure 19.

The monitor or detector 1632 may be any instrument which is adaptable to detect the intermediate oxidation product or products. It may, for example, comprise 5 a chromatography apparatus (such as GC and/or HPLC, for example), a UV spectrograph, an IR spectrograph, a visible light spectrograph, a mass spectrometer, a NMR instrument, a conductivity monitor, an ionization detector, a flame detector, any other suitable instrument, or a combination thereof.

10 In the case that the intermediate oxidation product is a non-volatile acid, it is preferable that the monitor or detector 1632 comprises a HPLC (High Pressure/Performance Liquid Chromatography instrument) in combination with a UV monitor. It is also preferable that the HPLC instrument has more than one columns, so that if the separation time in a column is longer than desired, 15 consecutive samples are introduced in different columns and a multiplicity of separations are conducted in parallel so that the interval between monitoring consecutive samples falls within desired limits. If it is desired to also analyze also non-polar organic moieties, it would be preferable to also include a gas chromatographic monitor or detector coupled with an appropriate monitor, such as 20 an ionization monitor, for example.

A combination of HPLC and GC may be utilized in case that polar and non-polar ingredients are involved

25 The methods and the devices of the instant invention are particularly suitable for oxidation reactions of organic compounds, wherein the major portion of the oxidation product is an oxidation intermediate different than CO, CO<sub>2</sub>, or a mixture thereof. One of the reasons why this is so, is that, due to the intricate criticalities of the present invention, the reaction rates, reaction homogeneity, yield, and other 30 important properties are considerably improved, while in the absence of said criticalities complete oxidation to CO/CO<sub>2</sub> would take place. Actually, the same conditions of atomization without said criticalities, are presently used in combustion engines of automobil s and other devices, to substantially completely oxidize

(combust or burn in other words) organic compounds such as gasoline to a mixture of CO/CO<sub>2</sub>.

In contrast, according to the present invention, if for example, the first 5 reactant is cyclohexane, the major portion of the oxidation product may be substantially cyclohexanol, cyclohexanone, cyclohexylhydroperoxide, caprolactone, adipic acid, the like, and mixtures thereof. Organic acids are preferable intermediate oxidation products.

10 The operation of the embodiments of the instant invention, will be discussed for any non-destructive oxidation encompassed by the claims, and at the same time it will be exemplified, by using cyclohexane as a first reactant, oxygen as the oxidant in the gas, and adipic acid as the intermediate oxidation product. The term "intermediate oxidation product", signifies that the oxidation stops before 15 substantially oxidizing the first reactant to carbon monoxide, carbon dioxide, or mixtures thereof.

Although three thermocouples and two sampling lines regarding conversion are shown, a smaller or larger number of these elements may be used. Minimally, 20 however, one thermocouple or one sample line has to be utilized. In addition, the device 1610 does not necessarily have to have all the elements shown, such as for example device(s) 1612a.

In operation, a first liquid containing the first reactant, cyclohexane for 25 example, enters the reaction chamber 1612 through line 1642 and it is atomized by the atomizer 1626 and nozzles 1627, in a manner to form a plurality of droplets 1648. The first liquid enters the atomizer at a desired atomization temperature, which in the case of cyclohexane is preferably in the range of 50-150° C, more 30 preferably in the range of 80 - 130° C, and even more preferably in the range of 90 - 120°. Other temperatures may of course be used depending on the particular circumstances. Atomization temperature of the first liquid is the temperature of the liquid just before it is atomized. The temperature of the just formed droplets may be the same or different than the atomization temperature. In the case of cyclohexane,

the first liquid also preferably contains a solvent, such as acetic acid, for example, a catalyst, such as a cobalt compound, soluble in the first liquid, for example, and an initiator, such as cyclohexanone, methylethylketone, acetaldehyde, the like, and mixtures thereof, for example. The pressure in the case of oxidation of cyclohexane to adipic acid should preferably be high enough to maintain the cyclohexane, solvents, initiators, etc., substantially in the liquid state. Although pressures even in excess of 1,000 psia are possible, pressures in the range of 100 to 400 psia are preferable, and pressures in the range of 150 to 300 psia more preferable.

At the same time that the first liquid is being atomized, a gas containing the oxidant, preferably oxygen in the case of cyclohexane, enters the chamber 1612 through the gas inlet feed line 1636, in the vicinity of the lower end 1616 of the chamber 1612. The gas, in addition to the oxidant, may also contain rather inert gases, such as nitrogen and/or carbon dioxide for example. Off gases, mixed with vapors of reactants, solvents, mist, and the like exit the reaction chamber through outlet gas line 1625.

As the droplets fall in a downwardly direction from the atomizer 1626, they start reacting with the oxidant, which is oxygen for example. The second liquid 1654 is removed, preferably continuously, through the liquid outlet 1622, and it is pumped through liquid outlet line 1624 by means of pump 1618.

If continuous operation is desired, the second liquid is initially recirculated through lines 1624a, 1624b, and 1642 to the atomizer 1626, until the conversion has reached a desired level. At that point, valve 1619 opens to a desired degree so that some of the second liquid, having the desired conversion level, passes to either the separator 1615 through lines 1624c and 1624d or to device 1612a through lines 1624c and 1624f for further treatment. The valve 1619a may direct the whole liquid portion from line 1624c to either the separator 1615 or the device 1612a, or partially to separator 1615 and partially to device 1612a, depending on the particular circumstances. The rest of the second liquid, which does not enter line 1624c, is recirculated to the atomizer 1626 through lines 1624b and 1642. Replenishment liquid containing first reactant, etc., enters the system through replenishment line

1641. The composition and amount of the replenishment liquid entering the system is such as to replenish, preferably quantitatively, the amounts of ingredients removed through line 1624c.

5        In case of a batch operation, as the device 1610 is supplied with adequate first liquid through replenishment line 1641, the whole amount of the second liquid is recirculated to the atomizer 1626 through lines 1624b and 1642, until a desired conversion has been reached, at which point the second liquid is removed from the reaction chamber 1612 through properly activated valve 1619 (and, if so desired, 10 valve 1619a) and line 1624c to enter separator 1615 or device 1612a, or partially separator 1615 and partially device 12a for further treatment. New first liquid enters the system through replenishment line 1641, and the cycle is repeated.

15        In the separator 1615, the intermediate oxidation product, adipic acid for example, is separated from the liquids by techniques well known to the art. In some occasions, other by-products of the oxidation may also be removed in the separator, if so desired. Reactants, solvents, catalysts, and the like, return to a recirculation tank (not shown) through line 1611. If at least part of the second liquid 1654 is at least partially directed to device 1612a, it may also be redirected to 20 separator 1615, after any treatment in the device 1612a, through line 1611a.

25        A part of the droplets 1648 fall onto thermocouple 60a, which in turn feeds the temperature information to the controller 1635 through input line 60a'. The atomization temperature and the temperature of the second liquid are also fed to the controller 1635 through input lines 1660' and 1660b', respectively. At the same time, part of the droplets also fall into the sample collector 1630, from where, they are directed to the conversion detector or monitor 1632, to be analyzed regarding conversion. If solids are present in the droplets, care should be taken to prevent clogging of liquid transporting lines by use of appropriate dilution, and the like. In 30 addition, a small stream of second liquid is directed to the conversion detector 1632 through line 1633' for analysis regarding conversion. As aforementioned, in the case of adipic or other acid formation, it is preferable that the monitor 1632 comprises a chromatography apparatus, which more preferably is a High

Performance (or Pressure) Liquid Chromatography apparatus (HPLC), and even more preferably combined with a GC (gas chromatography) apparatus. This system, as also mentioned earlier, may preferably have an adequate number of columns, so that it is capable of making a respective number of overlapping determinations of the intermediate oxidation product present in the or of the second liquid 1654, so that the respective conversion of the first reactant to intermediate reaction product is checked as frequently as desired in each particular case. If the column, for example, separates the intermediate oxidation product in 8 minutes, and the desired interval between determinations is 2 minutes in a particular case, four columns are needed.

Sampling of the liquid in other locations, may also be desirable, and it may be carried out in the same detector 1632 or in a different detector (not shown).

15 The information obtained in the conversion detector or monitor 1632 is fed to computerized controller 1635 through its input line 1631, where it is processed by well known to the art techniques along with information received through lines 1660', 1660a', and 1660b' regarding the respective temperatures.

20 The controller 1635 controls heat exchanger 1645 (not shown) or any of a plurality of means, mentioned earlier, which may be utilized to adjust any determinant, as described in detail in our co-pending applications. For purposes of simplicity, brevity, and clarity, the heat exchanger 1645, which exemplifies one means for adjusting the determinants to control the oxidation rate, will be discussed 25 here, with the understanding that the same principles apply regarding any other means.

It is preferable that in controlling the reaction rate, the temperature of thermocouple 1660, measuring the temperature inside the reactor, takes 30 precedence, followed by the atomization temperature of thermocouple 1660, and then followed by the temperature of the second liquid 1654, as measured by thermocouple 1660b. The conversion of first reactant to intermediate oxidation product in the sample collector 1630 takes then precedence, followed by the

conversion of first reactant to oxidation product as provided in the path of lines 1624a and 1633'. Although it is preferable, and sometimes critical, especially in the case of fast reactions or very long reaction chambers, to adjust more than one determinant for controlling the oxidation rate, there are other occasions, especially 5 in the case of relatively slow reactions, which permit the use of only single determinant. As a matter of fact, in the case of very fast reactions or very long reaction chambers, it is preferable to use a plurality of thermocouples 1660a and sample collectors 1630, so that the temperature and conversion are monitored in the whole length of the reaction chamber.

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The controller 1635 is preferably adapted, by well known to the art techniques, to make decisions regarding what action to take in order to adjust a determinant, not only by the absolute values of the measurements, but also by the differences of the absolute values and the rate that any change in determinant takes 15 place. For example, if the temperature difference between thermocouples 60 and 60a rises at a faster rate than desired, the controller will have to order more drastic measures than if the temperature in thermocouple 1660a albeit high, does not rise at a high rate, especially as compared to the temperature of thermocouple 1660. The same applies between thermocouples 1660a, if more thermocouples 1660a are 20 present, and between conversions and conversion changes from samples provided by different sample collectors 1630, if more sample collectors 1630 are available.

Assuming that at least one thermocouple 1660a is present, the controller 1635 makes decisions based on the temperature provided by thermocouple 60a 25 first. If that temperature is above the desired temperature range, heat exchanger 1645 is ordered by the controller 1635 to lower the temperature of the first liquid passing from line 1642 to the atomizer 1626. This change is preferably conducted in increments, preferably in the range of 10 to 50%, and more preferably in the range of 10 to 30% of the temperature at which the liquid enters the heat exchanger, as 30 measured by a thermocouple (not shown for purposes of clarity) and provided to controller 1635. However, other ranges may be more appropriate, depending on the particular conditions, materials, previous determination, and the like. For example, if a 10% decrease in temperature is found not to have an appreciable result, the

following increment may be 30%, for example. On the other hand, if a 10% decrease in the atomization distance results in an overwhelming change in temperature, the next increment may be 5%, for example, until the temperature falls within the desirable range, preferably in the most desirable range, and even 5 more preferably if it attains a value in the vicinity of its most preferred set value.

In the case of oxidation of cyclohexane to adipic acid, for example, the preferred temperature range is 50 - 150° C, more preferably 80 - 130° C, and even more preferably 90 - 120° C. Depending on the particular circumstances however, 10 other temperatures, considerably higher or considerably lower than the ones given above may be more suitable, even in the case of cyclohexane to adipic acid.

After the temperature is found to be within the most desired range, it continues to be monitored with a goal in most cases to stay somewhere in the 15 vicinity of the middle value of said most desired range. Continuous monitoring and control are, of course, highly desirable, since the conditions in the reaction chamber may vary, causing changes in the pre-coalescing temperature.

The desired range may be constant or it may vary with time, conversion, and 20 other desired parameters.

After the first determinant is within its desirable range, the other determinants may be directed toward their desirable ranges, one after the other in the order described above, for as long as they do not interfere with the first determinant. If the 25 first determinant is absent, the second determinant takes precedence, and the same technique is followed, until the second determinant falls within its predetermined range, as described above for the first determinant.

Usually, the predetermined range for thermocouple 1660 should be lower 30 than the range for thermocouple 1660a. The temperature changes shown by thermocouple 1660b are necessarily slower than the ones shown by thermocouple 1660a, due to the mass of the second liquid 1654. In case that the determinant is the temperature of thermocouple 1660b, it is important that the volume of the second

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liquid 1654 at the lower end 1616 of the reaction chamber 1612 is as small as possible to respond as fast as possible in temperature changes of the droplets in the reaction chamber 1612.

5 It is highly preferable that one temperature determinant and one conversion determinant are utilized at the same time for controlling the oxidation rate.

Fast oxidations and/or long reaction chambers, as already mentioned, may require more than one sample collector 1630, while slow oxidations and/or short 10 reaction chambers may rely only in conversion measured in the second liquid 1654 through line 1633'.

Conversion measurements between the initial location, which is between the atomizer and the point at which the lines 1641 and 1642 meet, and any subsequent 15 point before any recirculation or after any number of recirculations, taking into account any external influences, such as new additions and the like, for example, may be made, and the oxidation rate may be calculated therefrom. The controller 1635 gives orders to the heat exchanger 1645 from conversion data in a similar manner as it does from temperature data. Conversions per time interval of 20 measurement (in a single pass or any desired number of recirculations) may preferably be maintained between 0.05% and 80%, although other values may be appropriate, depending on the particular case. This is also true in the case of adipic acid formation, where in some occasions the values of conversion may be extremely small and in other occasions extremely large. The range of 0.05% to 80%, however, 25 still remains a preferable range.

Many catalysts used for the oxidation are transition metals having more than one valence states. Their major catalytic action is exhibited when they are at a higher valance state than their lowest valance state at which they exist as ions. One 30 good example is cobalt in the case of oxidation of cyclohexane to adipic acid. An initiation period before the oxidation starts has often been attributed by researches to the addition of cobalt ions at a valance state of II. The cobalt catalyst is added at valance state II because cobaltous acetate, for example, is more readily available

and it is less expensive than cobaltic acetate. Thus, it takes a period of time for the cobaltous ion to be oxidized to cobaltic ion and start acting as a catalyst according to methods in the art so far, unless cobalt II is used, or the cobalt II is preoxidized. Even then, it takes time to oxidize cobalt II to cobalt III ions, due to the small 5 interface provided by bubbling the gas through the solution.

In the case of the instant invention, this period of oxidation becomes considerably smaller because of the high surface area provided.

10 In addition, the cobaltous ion can be pre-oxidized to cobaltic ion.

As aforementioned, oxidations according to this invention, are non-destructive oxidations, wherein the oxidation product is different than carbon monoxide, carbon dioxide, and a mixture thereof. Of course, small amounts of these 15 compounds may be formed along with the oxidation product, which may be one product or a mixture of products.

Examples include, but of course, are not limited to

20 preparation of C<sub>5</sub> - C<sub>8</sub> aliphatic dibasic acids from the corresponding saturated cycloaliphatic hydrocarbons, such as for example preparation of adipic acid from cyclohexane;

25 preparation of C<sub>5</sub> - C<sub>8</sub> aliphatic dibasic acids from the corresponding ketones, alcohols, and hydroperoxides of saturated cycloaliphatic hydrocarbons, such as for example preparation of adipic acid from cyclohexanone, cyclohexanol, and cyclohexylhydroperoxide;

30 preparation of C<sub>5</sub> - C<sub>8</sub> cyclic ketones, alcohols, and hydroperoxides from the corresponding saturated cycloaliphatic hydrocarbons, such as for example preparation of cyclohexanone, cyclohexanol, and cyclohexylhydroperoxide from cyclohexane; and

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preparation of aromatic multi-acids from the corresponding multi-alkyl aromatic compounds, such as for example preparation of phthalic acid, isophthalic acid, and terephthalic acid from o-xylene, m-xylene and p-xylene, respectively.

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Regarding adipic acid, the preparation of which is especially suited to the methods and apparatuses of this invention, general information may be found in a plethora of U.S. Patents, among other references. These, include, but are not limited to:

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U.S. Patents 2,223,493; 2,589,648; 2,285,914; 3,231,608; 3,234,271; 3,361,806; 3,390,174; 3,530,185; 3,649,685; 3,657,334; 3,957,876; 3,987,100; 4,032,569; 4,105,856; 4,158,739 (glutaric acid); 4,263,453; 4,331,608; 4,606,863; 4,902,827; 5,221,800; 5,321,157; and 5,463,119.

15

Examples demonstrating the operation of the instant invention have been given for illustration purposes only, and should not be construed as limiting the scope of this invention in any way. In addition it should be stressed that the preferred embodiments discussed in detail hereinabove, as well as any other embodiments 20 encompassed within the limits of the instant invention, may be practiced individually, or in any combination thereof, according to common sense and/or expert opinion. Individual sections of the embodiments may also be practiced individually or in combination with other individual sections of embodiments or embodiments in their totality, according to the present invention. These combinations also lie within the 25 realm of the present invention. Furthermore, any attempted explanations in the discussion are only speculative and are not intended to narrow the limits of this invention.

In figures 1 to 18 of the drawing, numerals differing by 100 represent 30 elements which are either substantially the same or perform the same function. Therefore, in the case that one element has been defined once in a certain embodiment, its re-definition in other embodiments illustrated in these figures by the same numerals or numerals differing by 100 is not necessary, and it has been often

omitted in the above description for purposes of brevity. In Figure 19, this rule has not been followed for all numerals.

5 The words "inlet line" and "outlet line" have been used to signify lines adapted to transfer materials for the operation of the process, such as volatiles, intermediate oxidation products, off-gases, and the like, for example. The words "input line" and "output line" have been used to signify lines adapted to transmit signals, which are mostly electrical, but they could also be hydraulic, pneumatic, optical, acoustic, and the like, for example.

10

A diagonal arrow through an element denotes that the element is controlled through a line, preferably electrical, connected to the arrow.

15 Internal condensation according to this invention is condensation of condensibles, which takes place within the pressurized system and before pressure drop to about atmospheric pressure. Internal inside condensation is condensation in the reaction chamber

20 Condensibles are substances having a boiling point higher than 15° C, while non condensibles are substances that have a boiling point of 15° C and lower. It should be understood that when referring to condensibles, it is meant "mostly condensibles" and when referring to non-condensibles it is meant "mostly non-condensibles", since small amounts of one kind will be mixed with the other kind at substantially all times.

25

In cases where dilution or concentration of the droplets occurs as they travel from the atomizer to the sample collector, such dilution has to be taken into account in the calculation of pre-coalescing transient conversion in the appropriately programmed controller by monitoring the sources of dilution or concentration using 30 well known to the art techniques.

Response time between changing one variable or parameter and the result it brings about should also be taken into account, and the controller calibrated or

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programmed accordingly, by well known to the art techniques.

What is claimed is:

1. In a method of preparing an intermediate oxidation product from a first liquid containing a first reactant and a gas containing an oxidant;

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wherein the improvement comprises the steps of:

10 (a) atomizing the first liquid to form a plurality of droplets in the gas at an atomization temperature and at an atomization distance from a mass of a second liquid;

(b) causing a substantially non-destructive oxidation at an oxidation pressure between the first reactant and the oxidant to form the intermediate oxidation product;

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(c) coalescing the droplets into the mass of the second liquid; and

20

(d) controlling the substantially non-destructive oxidation by adjusting a parameter or determinant selected from a group consisting of atomization temperature, droplet temperature, temperature of the second liquid, pre-coalescing temperature of the droplets, transient temperature difference of the droplets, transient temperature sub-difference of the droplets, conversion of first reactant to intermediate product in the droplets, conversion of first reactant to intermediate product in the first liquid, conversion of first reactant to intermediate product in the second liquid, pre-coalescing transient conversion, and a combination thereof, to be within respective predetermined ranges.

25 30 30 2. A method as defined in claim 1, further comprising a step of separating the intermediate oxidation product from the second liquid.

3. A method as defined in claim 1, wherein the droplets contain a catalyst at a predetermined level, and adjusting of said parameter or determinant is

performed by a step of changing said predetermined level of catalyst.

4. A method as defined in claim 1, wherein the droplets have an average droplet diameter and are produced at a desired first flow rate, the gas flows at a second flow rate, the droplets contain volatile ingredients volatilizing at a volatilization rate, the first liquid contains first reactant at a first content, the gas contains oxidant at a second content, and adjusting of said parameter or determinant is performed by a step selected from a group consisting of changing the atomization temperature, changing the reaction pressure, changing the atomization distance, changing the average droplet diameter, changing the first flow rate, changing the second flow rate, changing the volatilization rate, changing the first content, changing the second content, and a combination thereof.

5. A method as defined in claim 1, wherein the pre-coalescing transient conversion is monitored by a chromatographic method.

6. A method as defined in claim 1, wherein a major portion of the oxidation product is an organic compound, the first reactant comprises an organic compound, and the oxidant is oxygen.

20

7. A method as defined in claim 6, wherein

25 the first reactant comprises a compound selected from a group consisting of cyclohexane, cyclohexanone, cyclohexylhydroperoxide, cyclohexanol, o-xylene, m-xylene, p-xylene, a mixture of at least two of cyclohexane, cyclohexanone, cyclohexanol, and cyclohexylhydroperoxide, and a mixture of at least two of o-xylene, p-xylene, and m-xylene.

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the oxidant comprises oxygen; and

a major portion of the intermediate oxidation product comprises a compound selected from a group consisting of adipic acid,

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cyclohexanol, cyclohexanone, cyclohexylhydroperoxide, phthalic acid, isophthalic acid, terephthalic, a mixture of at least two of adipic acid, cyclohexanone, cyclohexanol, and cyclohexylhydroperoxide, and a mixture of at least two of phthalic acid, isophthalic acid, and terephthalic acid.

5

8. A method as defined in claim 1, wherein the intermediate oxidation product is a solid, and the step of separating said intermediate oxidation product from the second liquid includes a step of filtering the intermediate oxidation product out of the second liquid.

9. A method as defined in claim 1, wherein the step of atomizing is performed by spraying the first liquid by an airless technique.

15 10. A method as defined in claim 1, further comprising a step of internally condensing condensibles substantially under reaction pressure.

11. A method as defined in claim 1, wherein the non-destructive oxidation is conducted in a reaction zone surrounded by a film or curtain of liquid.

20

12. A method as defined in claim 1, wherein the predetermined range of at least one determinant selected from a group consisting of conversion of first reactant to intermediate product in the droplets, conversion of first reactant to intermediate product in the first liquid, conversion of first reactant to intermediate product in the second liquid, and pre-coalescing transient conversion, is 0.05% to 25 80%.

13. A method as defined in claim 1, wherein the predetermined range of at least one determinant selected from the group consisting of atomization 30 temperature, droplet temperature, temperature of the second liquid, pre-coalescing temperature of the droplets, transient temperature difference of the droplets, and transient temperature sub-difference of the droplets, is 50 to 250° C.

14. A method as defined in claim 1, wherein the transient temperature difference is 0.1 to 100° C.

15. In a device for preparing a reaction product from a first liquid containing a first reactant and a gas containing a second reactant comprising a reaction chamber having an upper end, a lower end, a wall, and a reaction zone, in which zone the first liquid is brought in contact with the gas for reacting at a reaction pressure, wherein the improvement comprises:

10 (a) an atomizer disposed within the reaction chamber adapted to break the first liquid into a plurality of droplets within the gas at an atomization temperature in a manner that the droplets coalesce on a mass of a second liquid containing reaction product, the droplets having a pre-coalescing temperature before they coalesce, the mass of the second liquid having a second liquid surface, the atomizer being away from said second liquid surface at an atomization distance;

15 (b) at least one monitor selected from a group consisting of a first temperature monitor for measuring the atomization temperature, a second temperature monitor for measuring pre-coalescing temperature, and/or transient temperature difference, and/or transient temperature difference, and/or droplet temperature, and/or temperature of the second liquid, and a conversion detector for monitoring conversion of first reactant to intermediate product in the droplets, and/or conversion of first reactant to intermediate product in the first liquid, and/or conversion of first reactant to intermediate product in the second liquid, and/or pre-coalescing transient conversion, and a combination thereof; and

20 (c) a controller connected to at least one of the first temperature monitor, the second temperature monitor, and the conversion detector in order to obtain respective information, the controller being adapted to point a parameter or determinant selected from a group consisting of atomization temperature, droplet temperature, temperature of the second liquid, pre-

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coalescing temperature of the droplets, transient temperature difference of the droplets, transient temperature sub-difference of the droplets, conversion of first reactant to intermediate product in the droplets, conversion of first reactant to intermediate product in the first liquid, conversion of first reactant to intermediate product in the second liquid, pre-coalescing transient conversion, and a combination thereof, toward respective predetermined ranges.

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16. A device as defined in claim 15, further comprising a separator communicating with the reaction chamber for separating the reaction product from the second liquid.

17. A device as defined in claim 15, wherein the droplets have an average droplet diameter and are produced at a desired first flow rate, the gas flows at a second flow rate, the droplets contain volatile ingredients volatilizing at a volatilization rate, the first liquid contains first reactant at a first content, the gas contains second reactant at a second content, and the controller is adapted to point the determinant toward the predetermined range by changing a variable selected from a group consisting of changing the atomization temperature, changing the reaction pressure, changing the atomization distance, changing the average droplet diameter, changing the first flow rate, changing the second flow rate, changing the volatilization rate, changing the first content, changing the second content, and a combination thereof.

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18. A device as defined in claim 15, wherein the conversion detector comprises a chromatography apparatus.

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19. A device as defined in claim 15, wherein the atomizer is disposed toward the upper end, and directed toward the lower end at the atomization distance.

20. A device as defined in claim 19, wherein the atomizer is airless.

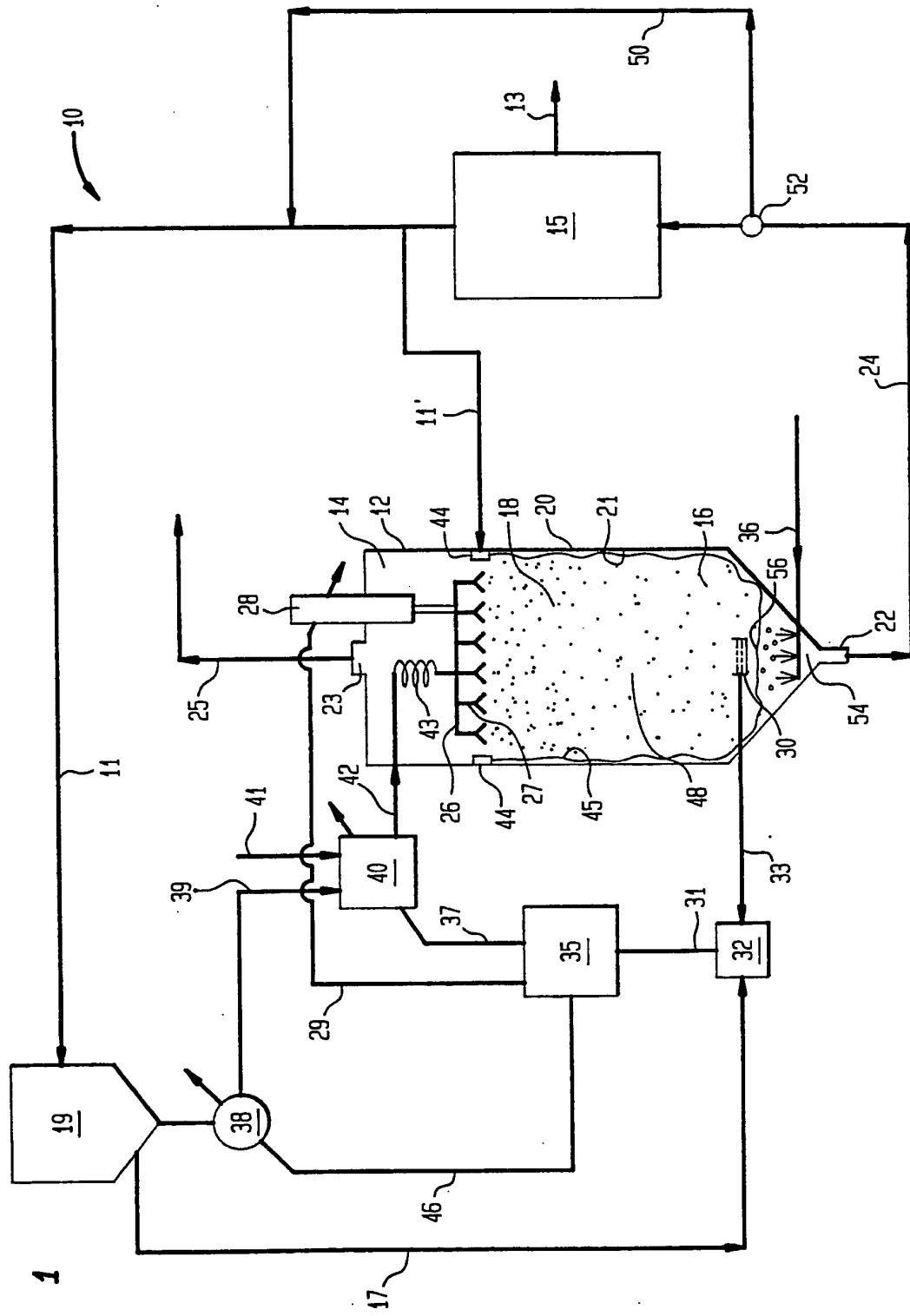
21. A device as defined in claim 15, further comprising a recirculation

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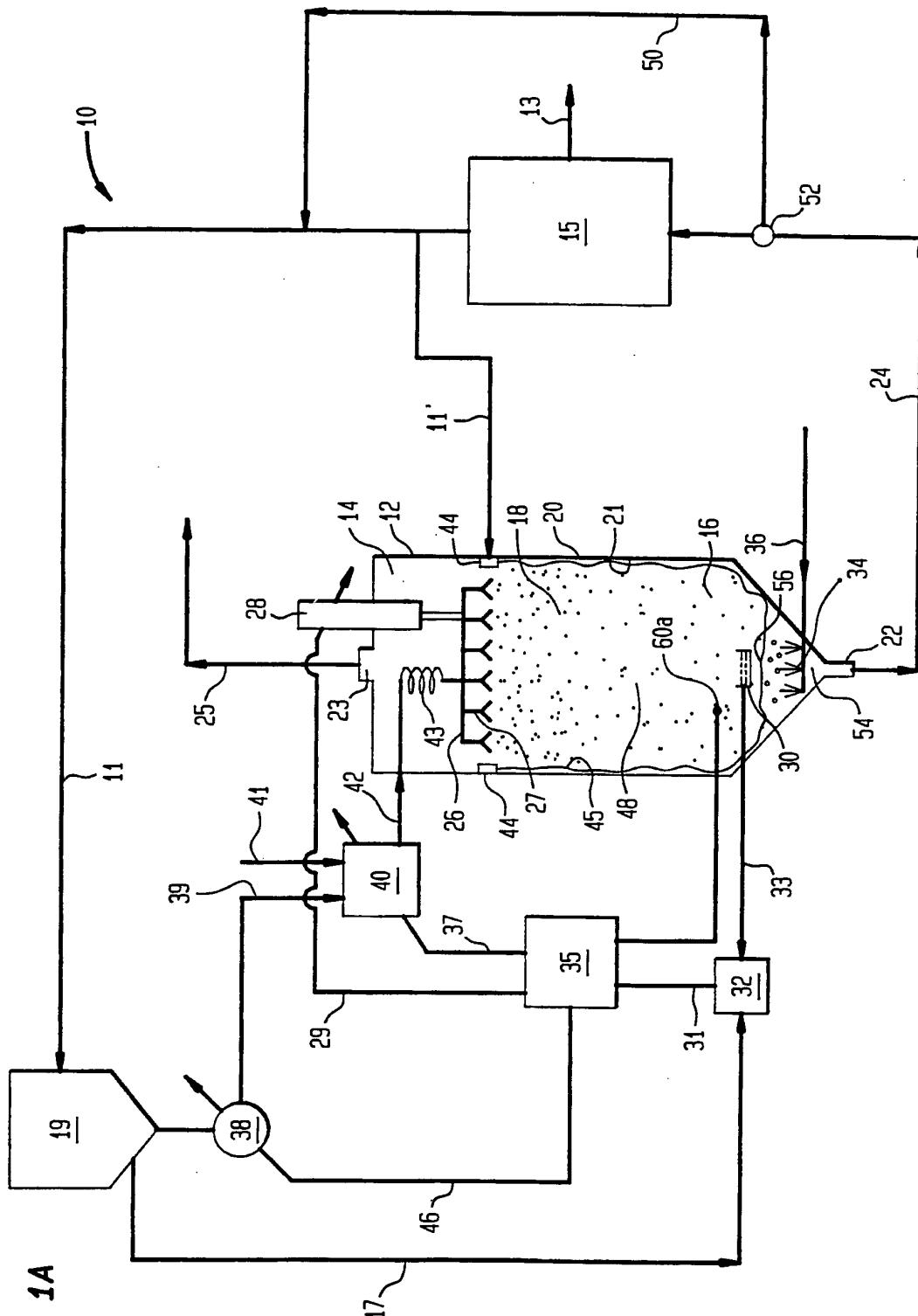
branch for recirculating at least part of the second liquid into the first liquid.

22. A device as defined in claim 15, further comprising means for condensing volatiles inside the reaction chamber.

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FIG. 2

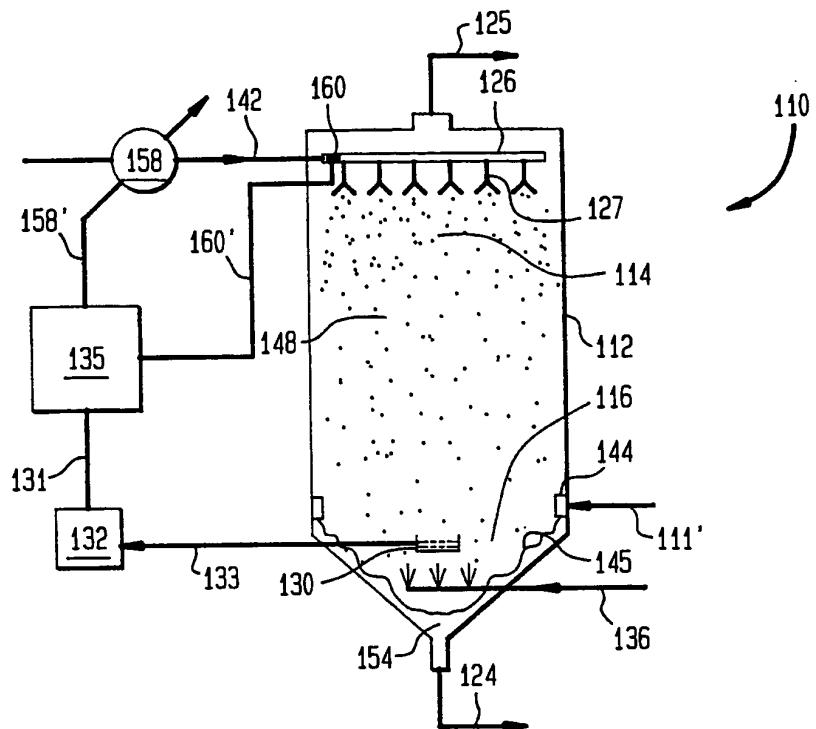
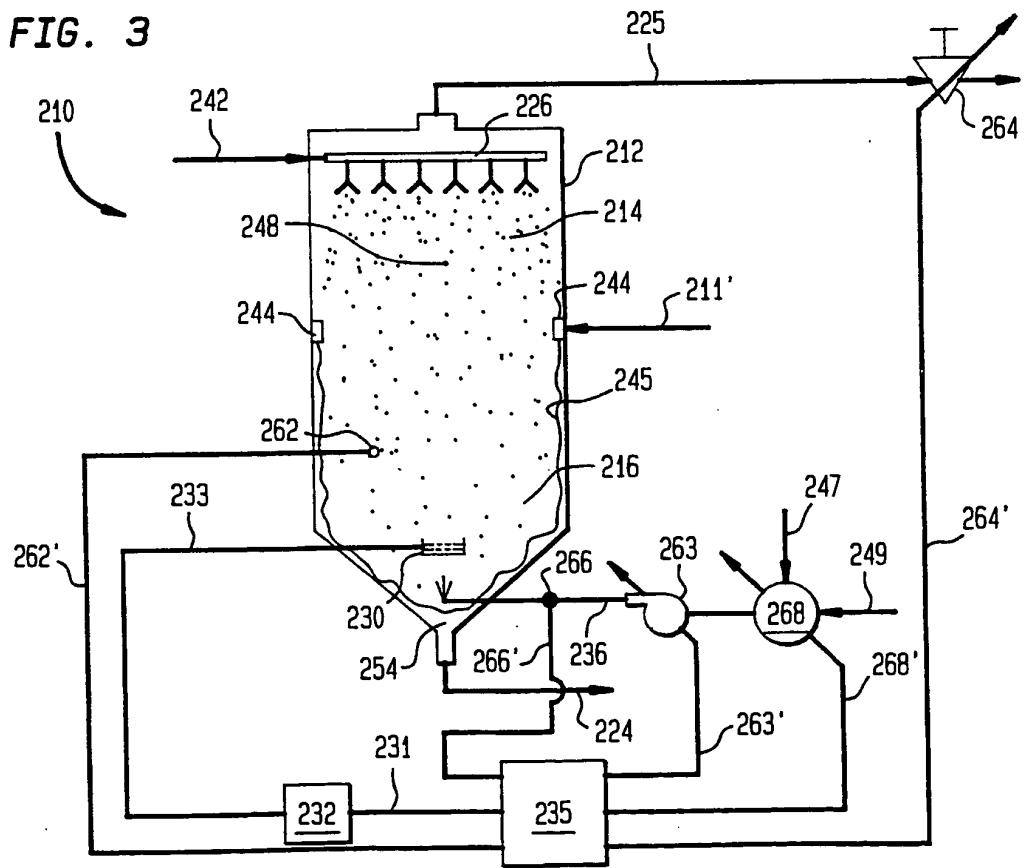


FIG. 3



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FIG. 2A

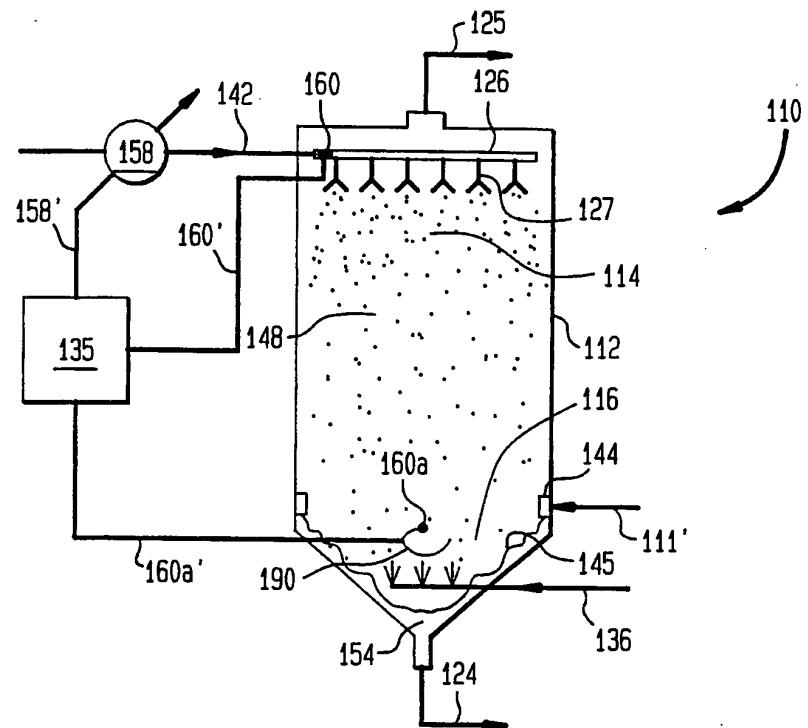
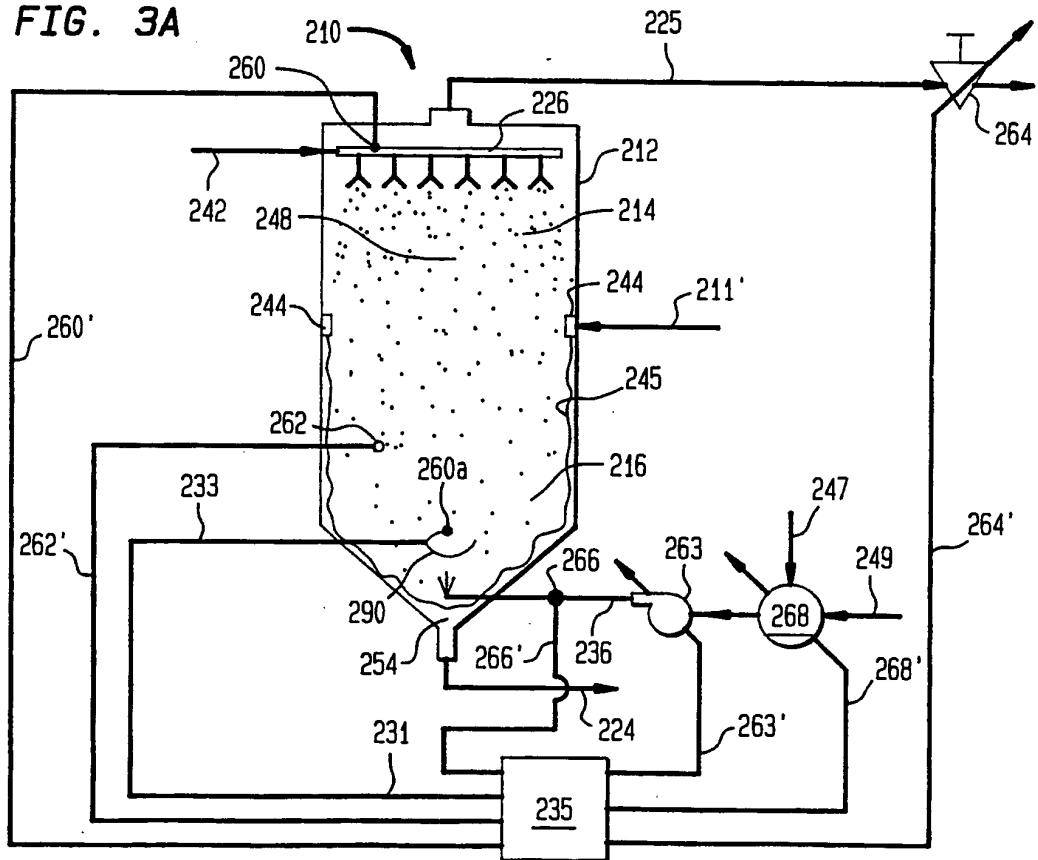


FIG. 3A



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FIG. 4A

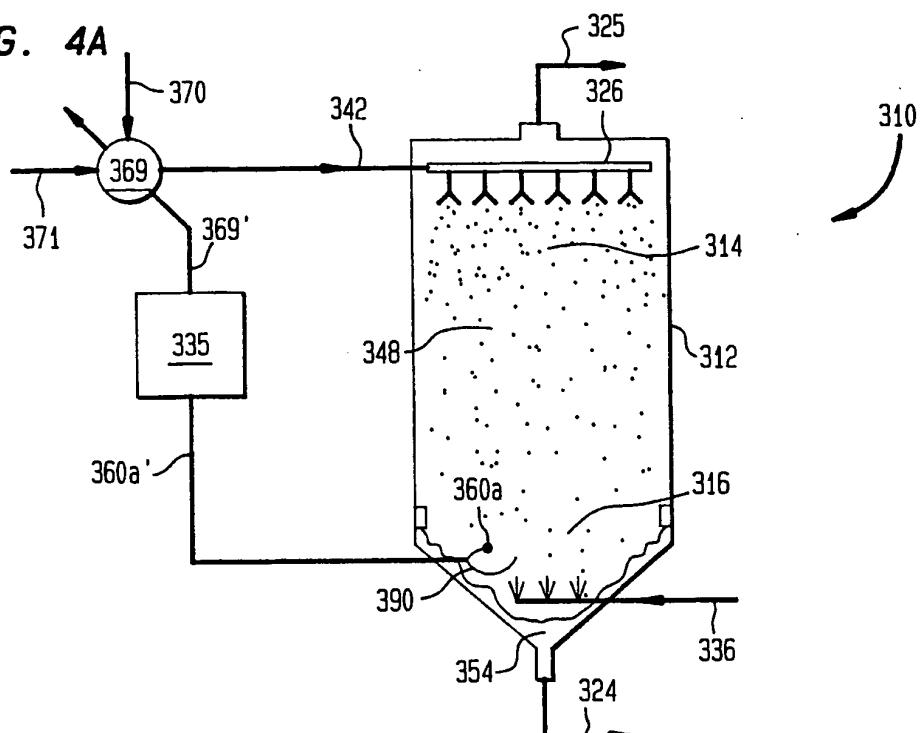
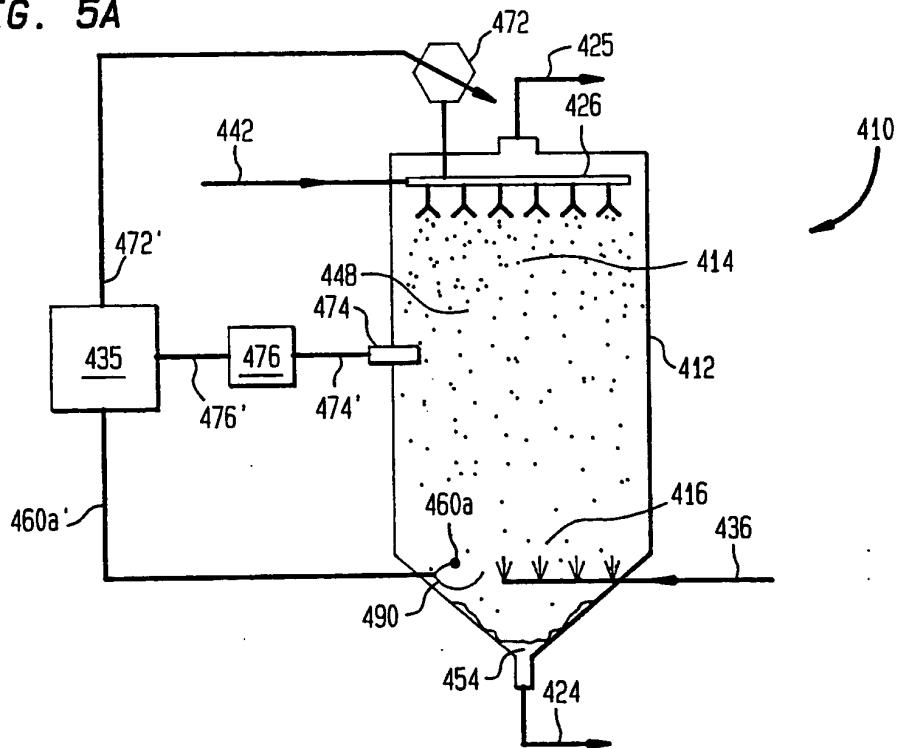


FIG. 5A



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FIG. 4

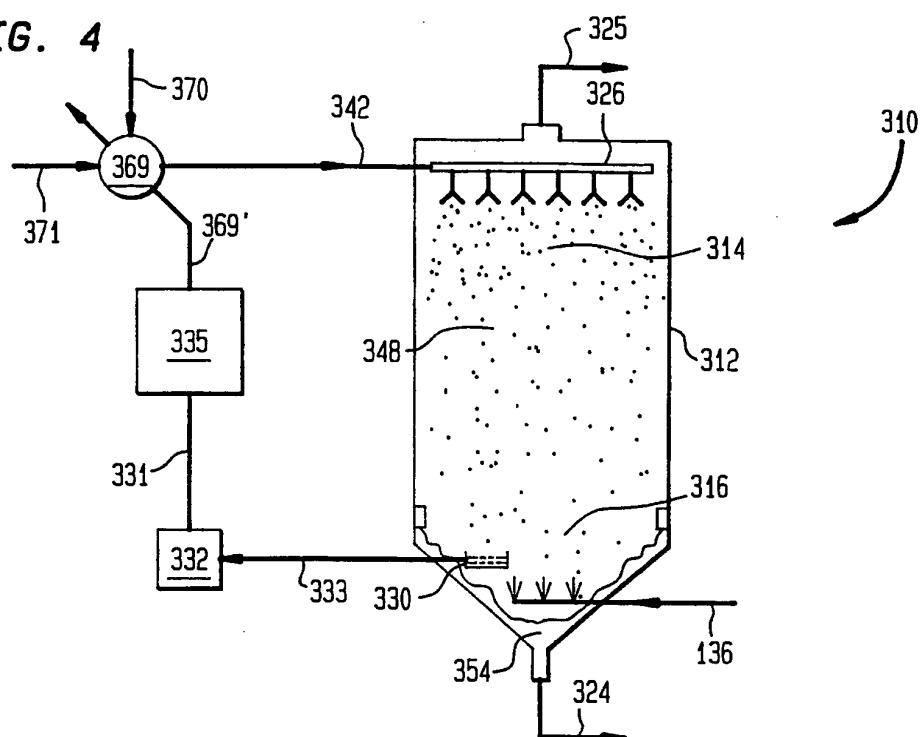
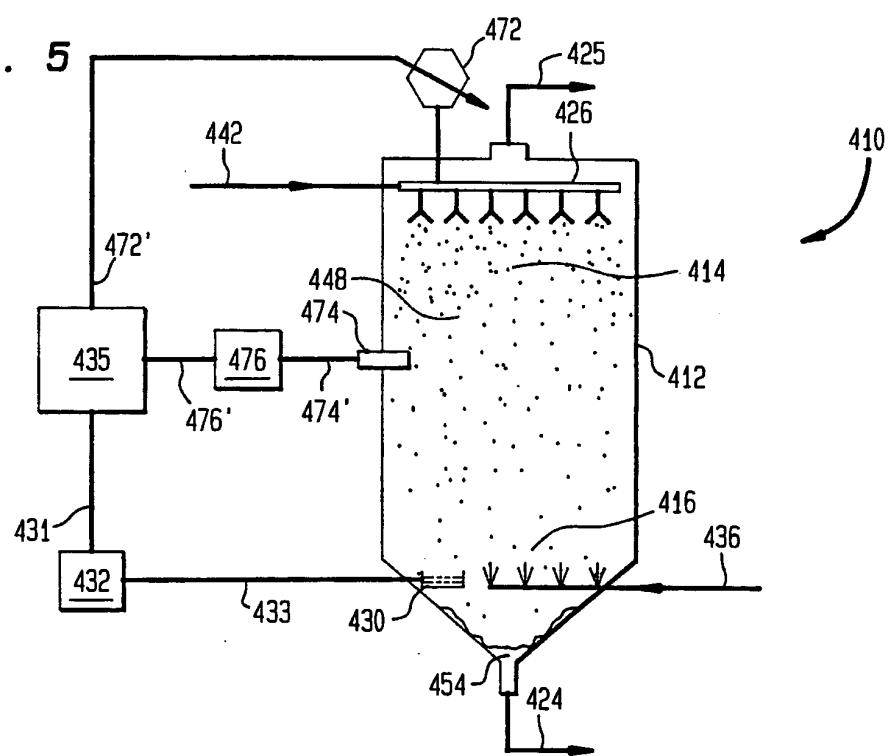


FIG. 5



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FIG. 6

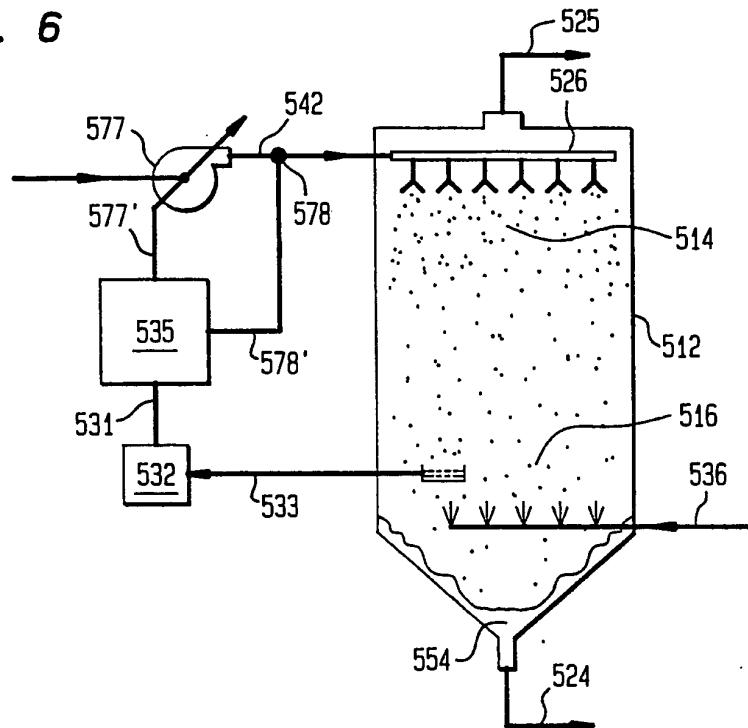
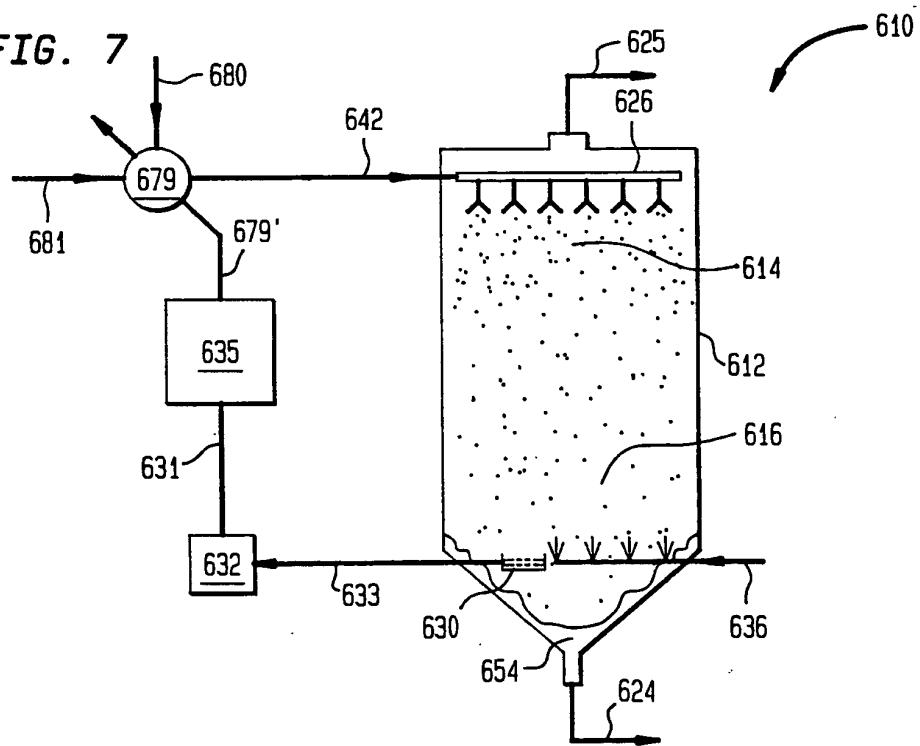


FIG. 7



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FIG. 6A

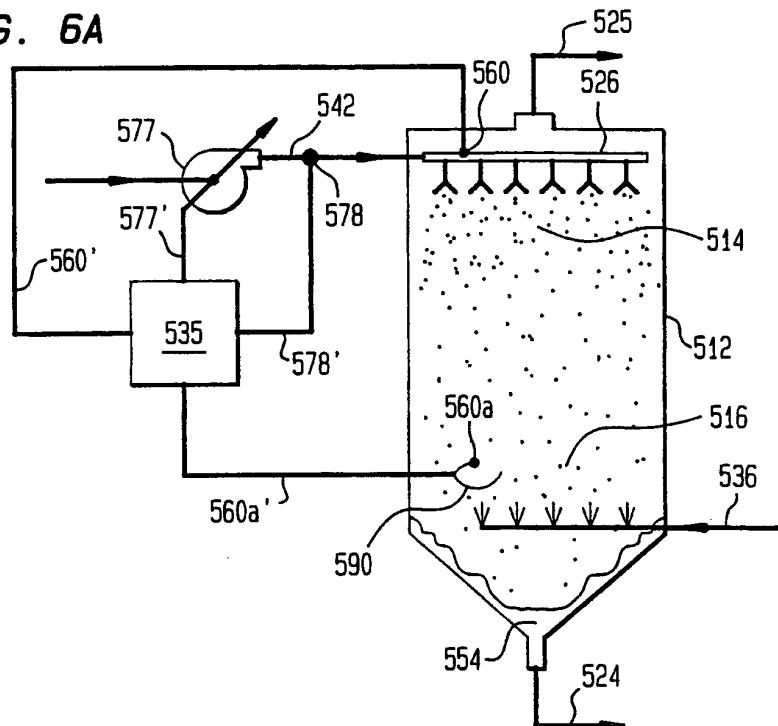
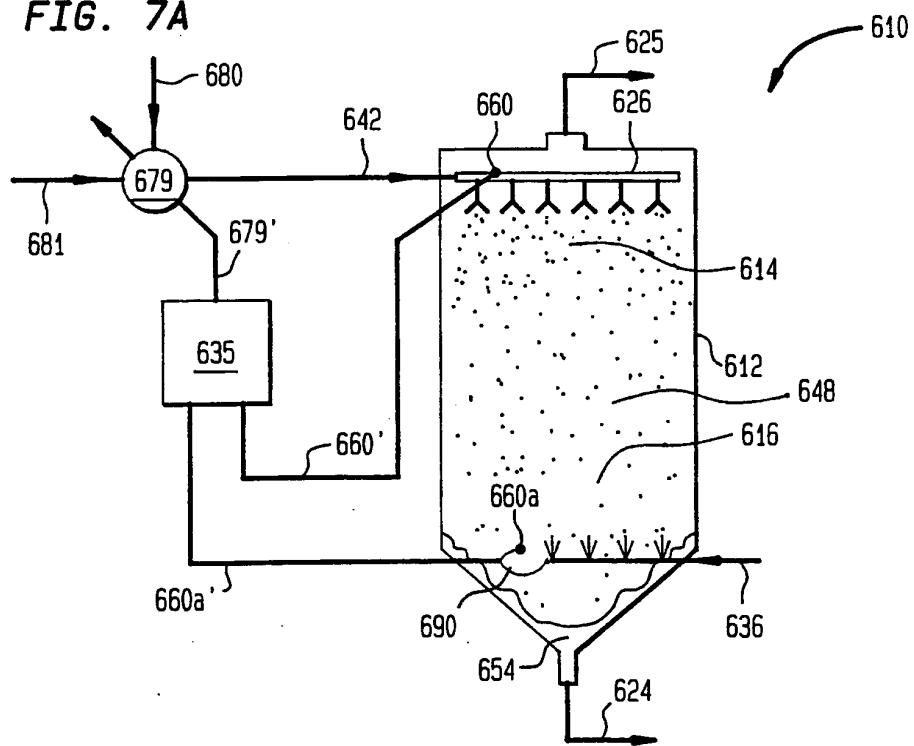
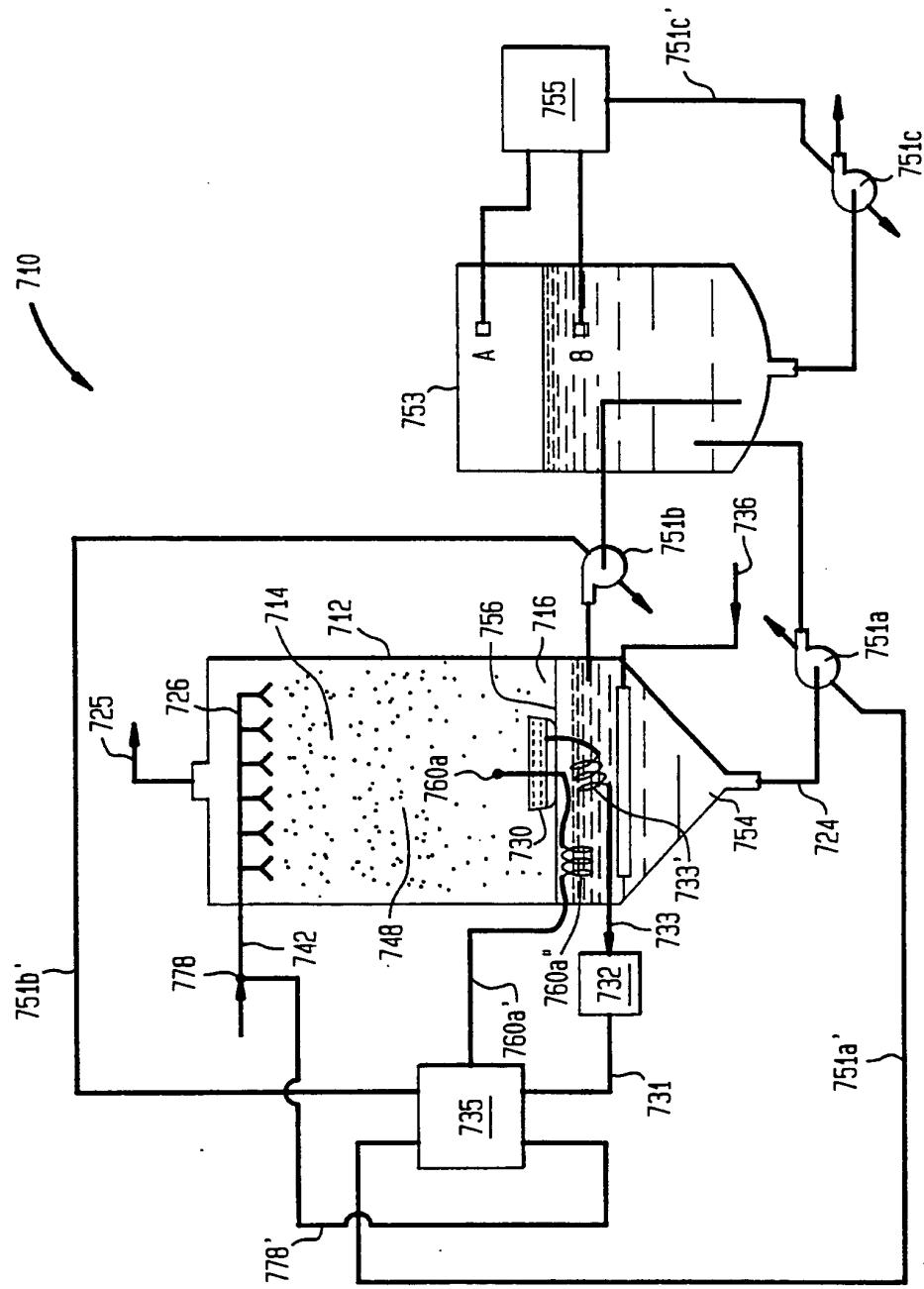


FIG. 7A



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FIG. 8



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FIG. 9

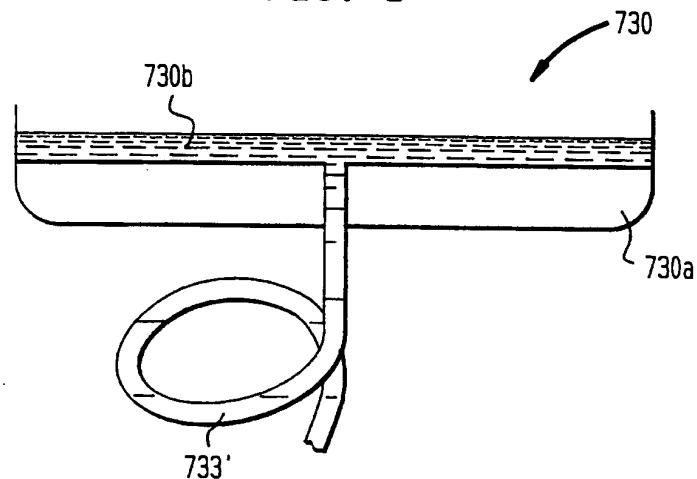
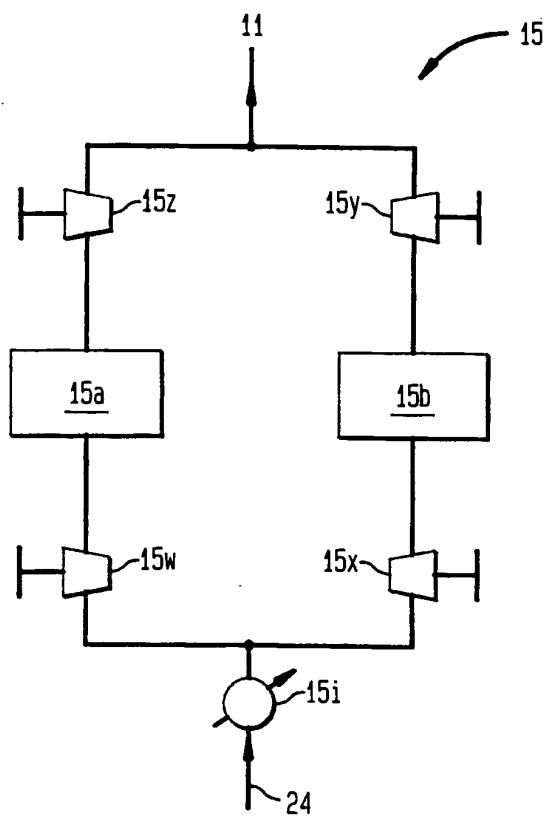
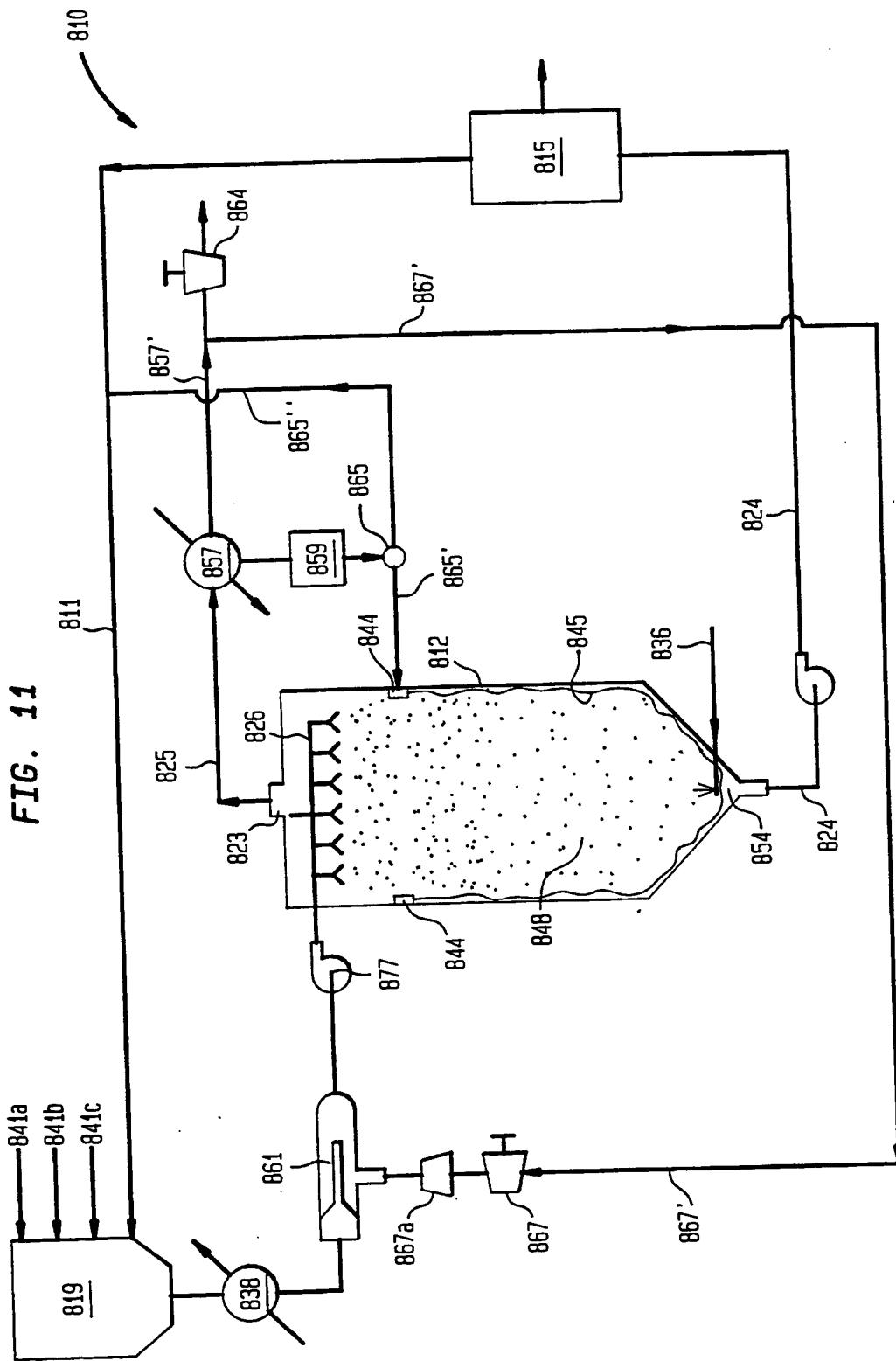


FIG. 10

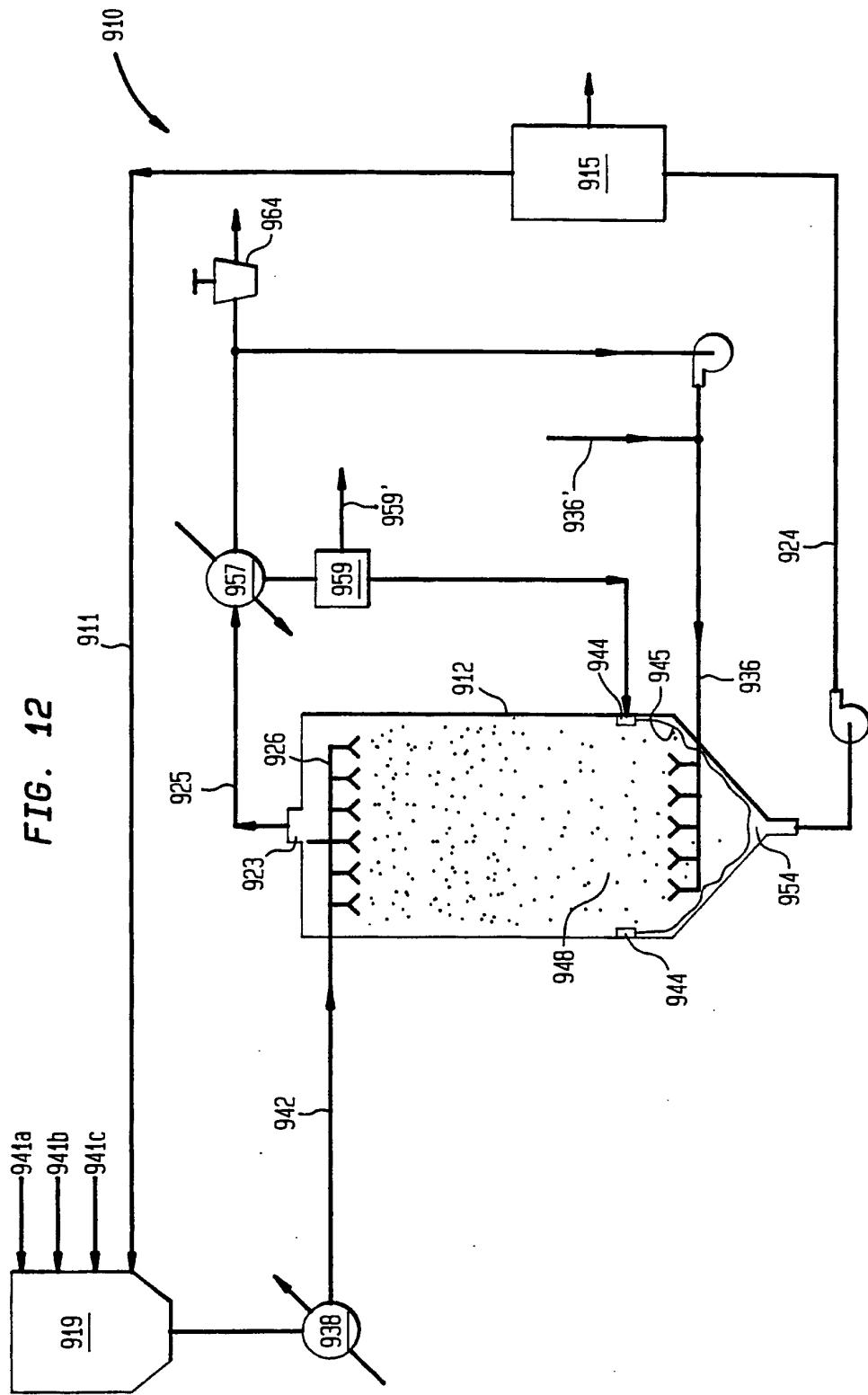


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FIG. 11

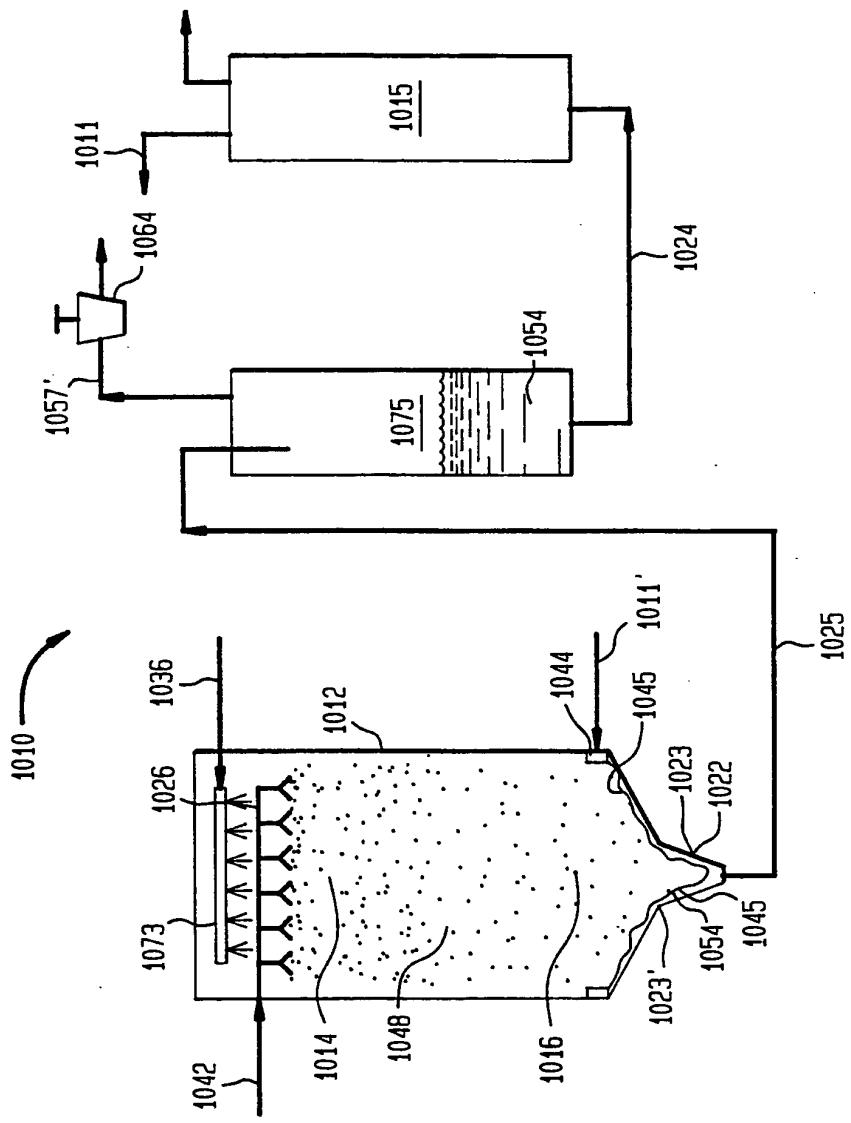


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FIG. 13



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FIG. 14

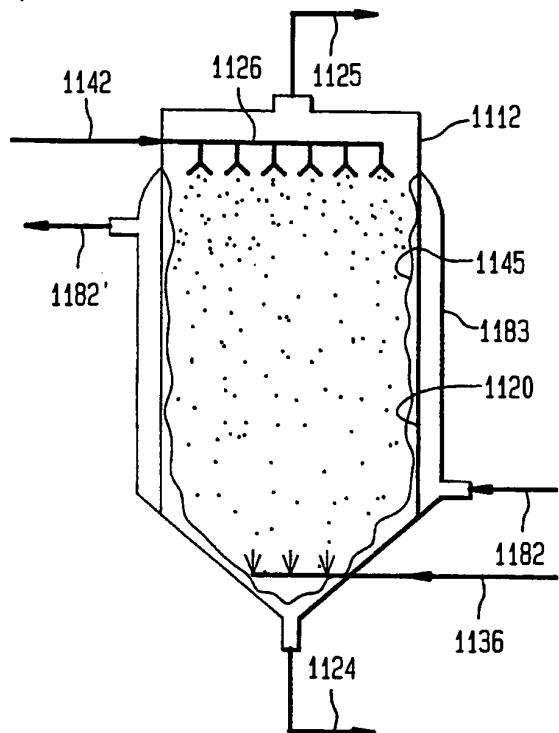
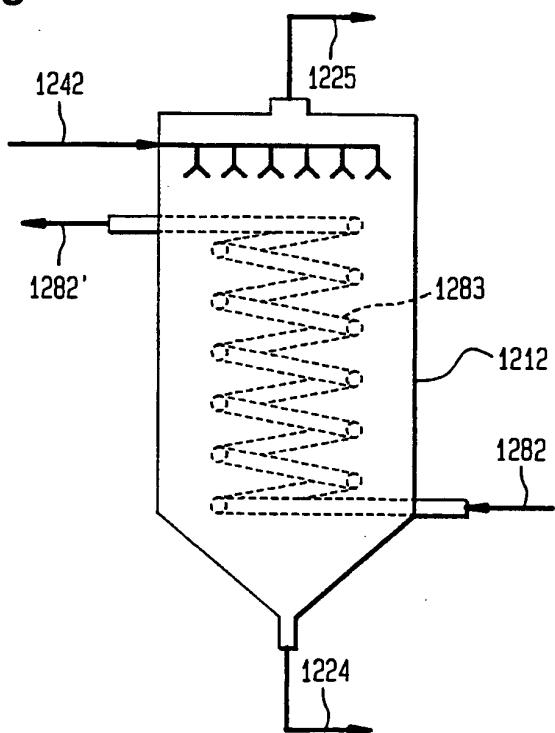
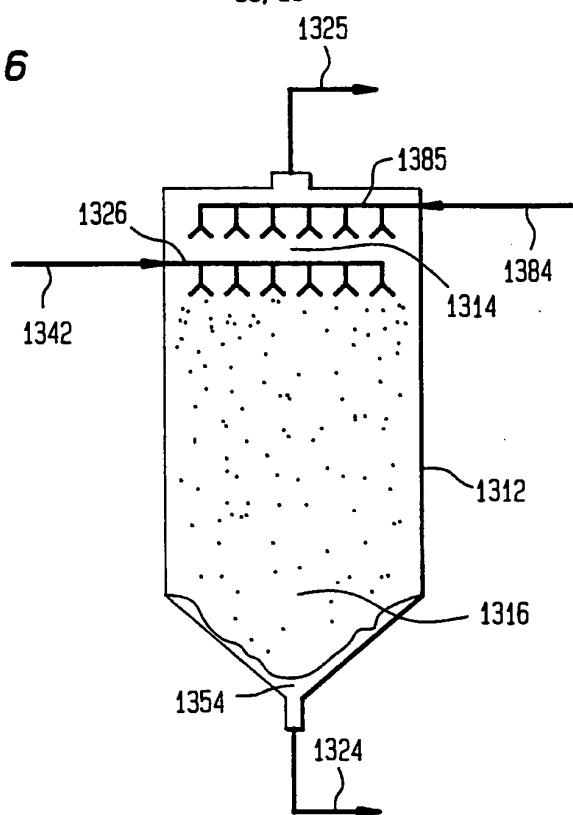


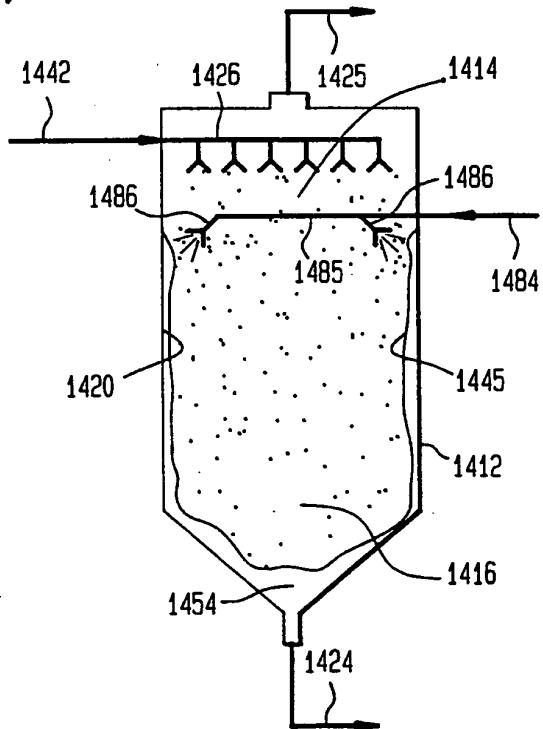
FIG. 15



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**FIG. 16**



**FIG. 17**



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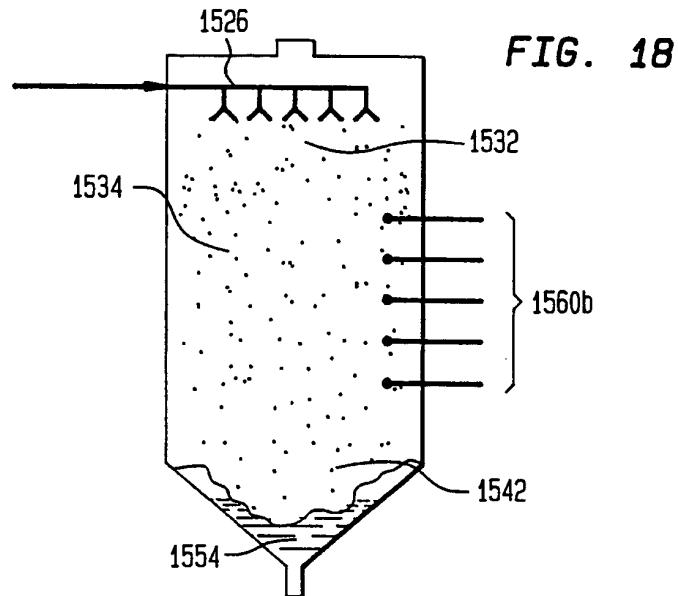
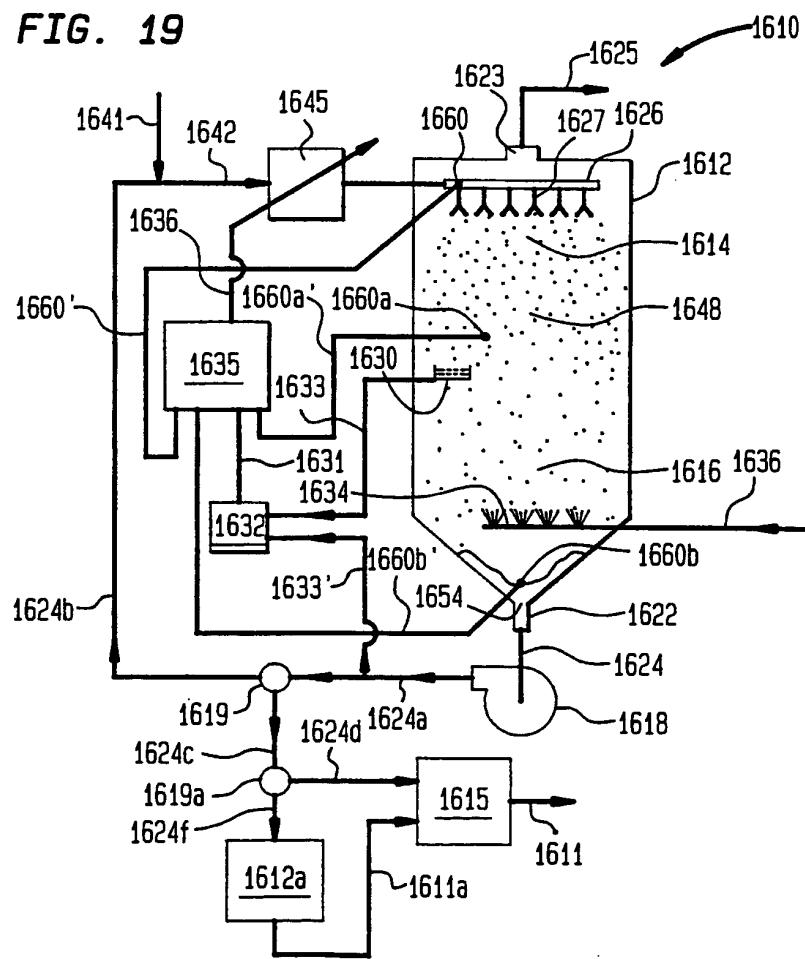


FIG. 18



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/07056

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07C 51/16

US CL : 562/413, 512.4, 528, 538, 543, 529; 568/357, 358, 570, 836

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 562/413, 512.4, 528, 538, 543, 529; 568/357, 358, 570, 836

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,221,800 (PARK ET AL) 22 June 1993.	1-22
A	US, A, 4,361,965 (GOUMONDY ET AL) 07 December 1982.	1-22
A	US, A, 5,270,019 (MELTON ET AL) 14 December 1993.	1-22
A	US, A, 5,321,157 (KOLLAR ET AL) 14 June 1994.	1-22

Further documents are listed in the continuation of Box C.

See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
• "A" document defining the general state of the art which is not considered to be of particular relevance		
• "E" earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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• "P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search  
28 JULY 1996

Date of mailing of the international search report

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